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ENANTIOMORPHISM IN MATHEMATICAL MODELS OF ORGANIC MOLECULES [1]

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Received February 10, 1948

INTRODUCTION

The enumeration of isomeric hydrocarbons is a study which has attracted the attention of mathematicians and chemists over a period of years. The earliest publication on this topic is that of Arthur Cayley. An historical account of developments prior to 1940 appears in an unpublished thesis written by this author.(1)

By far the most elegant treatment to be found is that of G. Pólya, who has solved the general problem posed in the following discussion:

Consider the n positions

$$x_1, x_2, \cdots, x_n$$

and a series of distinct objects, called a figure supply,

$$\phi', \phi'', \cdots, \phi^{(\lambda)}, \cdots,$$

where $\phi^{(\lambda)}$ contains three categories of colored spheres, α_λ red, β_λ blue, γ_λ yellow ($\lambda = 1,2,3,\cdots$). (Restriction to three categories is unessential, but is used at the moment for concreteness.) If to each position one attaches a single object, the entity of n positions with objects attached is defined as a configuration. (Use of an object in

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more than one position is permissible.)

The permutation

$$S = \begin{pmatrix} 1 & 2 & 3 & \cdots & n \\ P_1 & P_2 & P_3 & \cdots & P_n \end{pmatrix}$$

describes the interchange of the n objects in a configuration. If, with n distinct objects, the resulting configuration is considered equivalent to the original configuration, the permutation is called permissible.

Suppose one defines a certain group G of permissible permutations on n objects. Further, suppose the number of configurations with k red, l blue, and m yellow spheres is a_{klm}. The question then arises: How many configurations with r red, s blue, and t yellow spheres are there which are inequivalent with respect to G?

The method developed by Pólya in the solution of his problem has proved most convenient in this paper.[2] Another recent treatment which has been useful is that of Allen and Diehl.[3]

As special cases of his general solution, Pólya shows it may be applied to determine the number of certain (theoretically possible) isomeric chemical compounds. In the three dimensional chemical application, the n positions correspond to ends of free bonds extending from a certain skeletal framework, while the figures consist of chemical radicals which are to be attached to the free bonds, but are still free to rotate about the axis of the bond.

For example, in the alkene series, the skeletal framework is represented by

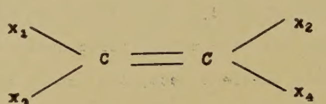


Figure 1

where the four bonds extending to the x_i are in the plane of the paper, and the four positions labelled x_1, x_2, x_3, x_4, are thought of as at the corners

of a rectangle. The double bond between the carbons is rigid, and the entire skeletal framework, without the figures attached, has the plane of the paper as a plane of symmetry.

The figure supply consists of the alkyl radicals or hydrogens. If the resulting configuration is to be superimposable on the original, the only permissible permutations are

$$I, \quad (12)(34), \quad (13)(24), \quad (14)(23).$$

The isomers enumerated in this case are known as stereoisomers, and since the discussion relates to the alkenes, we get the number of stereoisomeric alekenes by using Pólya's method.

From the point of view of the chemist, an important class of organic compounds are those steroisomers which are optically active. The theoretical criterion for optical activity due to molecular structure is that the mathematical three dimensional model of the molecule shall be non-superimposable on its mirror image. (Such non-superimposability is called enantiomorphism, and the molecules such models describe are called enantiomorphs.)

In the three dimensional chemical application, the figure supply necessarily contains objects (radicals) which are non-superimposable on their mirror images. Reflection of such objects through a plane mirror can not be described simply in terms of an interchange of n objects in in the configuration. (As a simple example, two right handed gloves on reflection in a plane mirror not only change positions, but each becomes a left handed glove.)

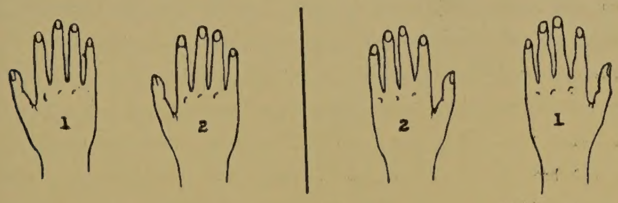


Figure 2.

Since Pólya's problem requires definition of a permissible group of interchanges, the general solution of Pólya is not directly applicable to the problem of determining the number of theoretically possible enantiomorphs.

It is the purpose of this paper to develop methods of abstracting new skeletal frameworks and new figure supplies from those used in the stereoisomeric applications, in order to make the Pólya solution adaptable to the enumeration of enantiomorphs.

Although the writer has not obtained a general solution, the discussion being limited to three types of organic compounds, the monohydroxy saturated alcohols, the alkenes, and the paraffines, it is hoped that the abstraction methods used will prove valuable in further investigation.

CHEMICAL ASPECTS

In much of the discussion of optical activity and its basis in molecular structure there is confusion and inaccuracy. This is due in part to excessive use of the "asymmetric carbon," in part to inexactness in its definition. An asymmetric carbon atom is one whose bonds are attached to four "different" radicals. For clear reasoning it is all-important to know whether "different" radicals must differ topologically or may differ only spatially - whether, in other words, the distinction of right and left handed orientations is irrelevant or not. Evidently, then, there are two distinct definitions of the asymmetric carbon - a fact rarely recognized.

And whichever definition is used, the absence of asymmetric carbons has little causal connection with optical activity. This activity, in so far as the structure of a single molecule is its cause, comes from the fact of the molecule's not being superimposable on its mirror image - a situation forbidding any plane of symmetry. Now a molecule can perfectly well have such a plane, yet have no symmetric carbon - as when a single bond unites two radicals, which are devoid of symmetric carbons and which are mirror images of each other. And a molecule can have no

single asymmetric carbon, and still be active - as, for instance, an allene with four topologically different substituents, none of which has an asymmetric carbon. (Here the presence of rings - the double carbon bonds - is important.)

As an example of imperfect consideration of isomerism let us note certain passages by Shriner and Adams.[4] On pages 224 and 225 of the second edition, four models of the molecules Ca_4, Ca_3b, Ca_2bc, Ca_2b_2, (Figures 3,4,5,6) are shown,

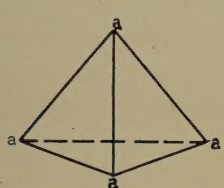


Figure 3

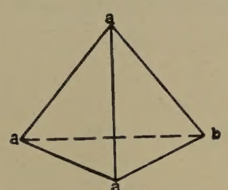


Figure 4

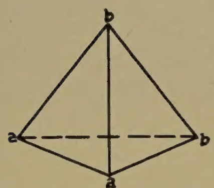


Figure 5

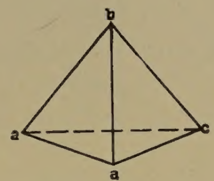


Figure 6

together with the statement that "the mirror images of the models represented by Figures 3, 4, 5, 6 are identical with the originals, and no optical isomerism is possible. That such a general statement is incorrect can be shown as follows: Among the chemical radicals denoted by a, b, c, it is desirable to distinguish between two cases, that in which the radicals are superimposable on their own mirror images, and that in which they are not. In the first case it is convenient to describe the radical as R_i where i is assigned some integral value. If two radicals, R_i and R_j, are considered identical, it is necessary and sufficient that one assign the same value to i and j. In the second case it is convenient to describe the radicals as d_i or l_i, where again i is assigned some integral value. With a pair of radicals, each of which is the

non-superimposable mirror image of the other, one is described as d_i and the other as l_i, where both have the same integral value assigned to i.

Now consider the case Ca_4. If a = R_1, one obtains

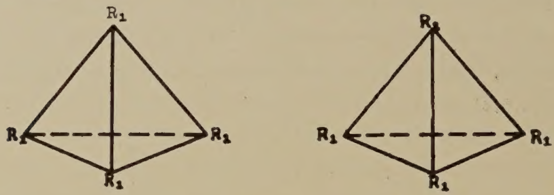


Figure 7

but if a = d_1, one obtains,

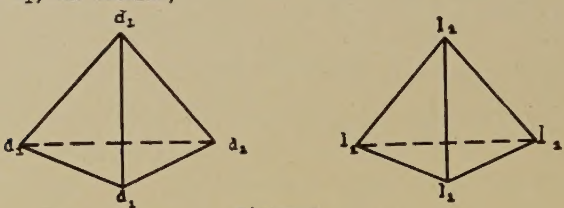


Figure 8

and certainly the mirror image is non-superimposable on the original. In this case, even the spatial identity of the four radicals d does not guarantee optical inactivity - all the less does their topological identity do so. Similar treatment applied to the molecules Ca_3b, Ca_2bc, and Ca_2b_2 adds conclusive evidence to refute the general statement quoted above.

In general Shriner and Adams seem to use the topological definition of "difference." For example, on page 234 in the discussion of dextro- and levo-trihydroxyglutaric acid, one finds "In these models the central carbon B is <u>not</u> asymmetric since two of the groups attached to it are identical." Yet on page 235, in the discussion of meso-trihydroxyglutaric acid, one finds "A carbon atom of this type, although it holds four different groups, possesses a plane of symmetry because of the fact that two of these groups are mirror images of each other. It is, therefore, not <u>truly</u> asymmetric and hence is termed pseudoasymmetric." At this

point Adams and Shriner are obviously thinking of difference of groups in orientation only.

Further examples of questionable treatment of steroisomerism are found in the works of A. Bernthsen[6], W. T. Caldwell[7], Julius B. Cohen[8], Charles S. Gibson[9], Paul Karrer[10], George Holmes Richter[11]. Jaeger's conclusion seems inescapable: "From the theoretical point of view the asymmetric carbon atom is a superfluous conception; it may be preserved, however, as a guide to the practical chemist in deciding whether or not he shall look for optical isomerides. The doctrine of the asymmetric atom has done splendid service in stimulating innumerable experimental investigations, and in this capacity has been a necessary link in developing our sterochemical views. After coming so far, however, and standing now on the shoulders of the earlier workers, we must have a broader outlook than our predecessors. We must now acknowledge that the conception of the asymmetric atom embraces only a special, and not even a simple, case of the much more general view, namely, the symmetry relations of the molecule in its totality; and we should not stick too persistently to the more restricted and often rather vague notion of 'asymmetric' atoms. It is increasingly necessary--especially with the experience gathered during the last ten years--to realize that the doctrine of the asymmetric atom should no longer be regarded as a fundamental concept in our views of the connection between molecular composition and optical activity of solutions."[5]

THE PÓLYA METHOD

If the figure $\phi^{(\lambda)}$ has α_λ red spheres, β_λ blue spheres, and γ_λ yellow spheres, it is said to have <u>spherical content</u> $(\alpha_\lambda, \beta_\lambda, \gamma_\lambda)$. There may be several figures in the supply which have the same spherical content. Designating the number of figures of spherical content (k,l,m) by a_{klm}, one calls the power series

$$(1)\quad \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} a_{klm}x^k y^l z^m = \sum_{k,l,m} a_{klm}x^k y^l z^m = f(x,y,z)$$

the enumerative power series of the figure supply.

Any permutation from the group of permissible interchanges may be described as a permutation of type $[j_1, j_2, \cdots, j_s]$. This means it contains j_1 cycles of first order, j_2 cycles of second order, $\cdots$, and j_s cycles of s^{th} order, where

$$(2) \qquad 1j_1 + 2j_2 + 3j_3 + \cdots + sj_s = n,$$

(n being the degree of the group).

The number of permutations of type $[j_1, j_2, \cdots, j_s]$ in the group is designated by $h_{j_1 j_2 \cdots j_s}$. Letting $f_1, f_2, f_3, \cdots, f_s$ be independent variables, the polynomial

$$\frac{1}{h} \sum_{(j)} h_{j_1 j_2 \cdots j_s} f_1^{j_1} f_2^{j_2} \cdots f_s^{j_s} \qquad (h = \sum_{(j)} h_{j_1 j_2 \cdots j_s})$$

is called the cyclic indicator of the group. (In the cyclic indicator, the summation is to be extended over all non-negative integral solutions of (2) .

The Pólya method calls for introducing the enumerative power series of the figure supply into the cyclic indicator. In order to do this it is necessary to have a second meaning for f_n. When introducing $f(x,y,z)$ into the cyclic indicator, one must use

$$\begin{aligned} f_1 &= f(x,y,z) \\ f_2 &= f(x^2,y^2,z^2) \\ &\cdots\cdots\cdots \\ f_n &= f(x^n,y^n,z^n). \end{aligned}$$

It is then possible to express the Pólya method as follows: In order to obtain the enumerative power series of the configurations inequivalent with respect to the group H, one must introduce the enumerative power series of the figure supply into the cyclic indicator of the group.

(Restriction to three categories of spheres has been continued for the sake of concreteness.)

Pólya speaks of two cases in which the cyclic indicator of a group built up out of several given groups is related in a distinct manner to

the cyclic indicators of the given groups, the "direct product", G x H, and the "Kranz" (wreath), G[H]. Of these, only the former is needed in the present problem.

With G x H, one arranges a permutation of the objects $x_1, x_2, \cdots, x_r, y_1, y_2, \cdots, y_s$ to correspond to a pair of permutations (one from G operating on the x's, one from H operating on the y's) in the following manner,

$$\begin{pmatrix} x_1 & x_2 & \cdots & x_r & y_1 & y_2 & \cdots & y_s \\ x'_1 & x'_2 & \cdots & x'_r & y'_1 & y'_2 & \cdots & y'_s \end{pmatrix}$$

These built-up permutations form a permutation group, G x H. If ϕ is the cyclic indicator of G and ψ is the cyclic indicator of H, then $\phi\psi$ is the cyclic indicator of G x H. (The figure supply for the x's may even be distinct from that for the y's). A direct product G x H x K ··· has cyclic indicator $\phi\psi\chi \cdots$.

THE PROBLEM

Since all authors are not in agreement as to the meaning of the term "stereoisomer", it is necessary to define what is meant by it in this paper.

A stereoisomer means any molecule whose three dimensional space model possesses a specific structure. (It need not possess a non-superimposable mirror image.) The number of stereoisomers of a given type with a given structural formula (e.g., stereoisomeric alcohols with structural formula $C_7H_{15}OH$) is the number of non-superimposable space models which correspond to the given type and given structural formula. (I.e., with the above example, it is the number of non-superimposable space models of alcohols whose structural formulas are all the same, namely $C_7H_{15}OH$.)

It is quite natural to divide the stereoisomers into two classes:

(1) Those whose models are superimposable on their own mirror images are called non-enantiomorphs.

(2) Those whose models are not superimposable on their own mirror images are called enantiomorphs. (These correspond to the optically

active molecules.)

Our problem is to find a way of using the Pólya method to determine the number of enantiomorphic and non-enantiomorphic alcohols (saturated mono-hydroxy), alkenes, and paraffines.

Further discussion is divided into the following sections:

Application of the Pólya method to determine the functional equations for enumeration of stereoisomeric alcohols, alkenes, and paraffines.

Abstraction of new skeletal frameworks and new figure supplies from those used in stereoisomeric applications, and determination of functional equations for enumeration of enantiomorphs and non-enantiomorphs.

Function theoretic discussion of the functional equations, and investigation of the asymptotic behavior of the coefficients determined thereby.

In the applications of his general solution to chemical problems, Pólya has treated the cases of the stereoisomeric alcohols and the stereoisomeric paraffines. However, since the methods used (in the present paper) to treat the enantiomorphs and non-enantiomorphs assume a prior knowledge of the results on the stereoisomers, it has seemed desirable to include an account of the stereoisomers in the discussion.

FUNCTIONAL EQUATIONS FOR STEREOISOMERS

A. Alcohols

In the three dimensional model of the alcohols, the skeletal framework consists of a regular tetrahedron, with a carbon atom at the center (not shown in Figure 9), with an OH group attached to one vertex, and with each of the other three vertices available to attach an alkyl radical or a hydrogen atom.

The group of permissible permutations, which allow superposition of

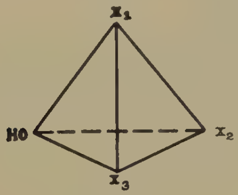


Figure 9

the resulting configuration on the original, is

$$I = (1)(2)(3), \quad (123), (132).$$

Since this group consists of one permutation of type [3,0,0] and two permutations of type [0,0,1], the cyclic indicator is

$$\frac{f_1^3 + 2f_3}{3}.$$

With the alcohols it is unnecessary to have a variable in the enumerative power series to account for the hydrogens used, since n carbons necessitate exactly (2n + 1) hydrogen atoms, exclusive of the one in the OH group. Hence, one may let

$$s(x) = \sum_{n=0}^{\infty} S_n x^n$$

represent the enumerative power series of the stereoisomeric alcohols, where n is the number of carbon atoms.

Since the alkyl radicals are equivalent to alcohols with the OH group replaced by a free bond, it is evident that the number of alkyl radicals is equal to the number of alcohols. Consequently the enumerative power series for the alcohols is identical with thet for the alkly radicals, which, along with the hydrogen atom, make up the figure supply.

In order to include the hydrogen atom in the enumerative power series of the figure supply, one need only let HOH be counted as an alcohol with no carbons. This necessitates giving S_0 the value 1. Keeping this in mind and applying the Pólya method, we find

$$(3) \qquad s(x) = 1 + x\,\frac{s(x)^3 + 2s(x^3)}{3}.$$

B. Alkenes

In the three dimensional model of the alkenes, the skeletal framework consists of two carbon atoms connected rigidly by a double bond, with the four free bonds extending out to what might be considered the vertices of a rectangle. The four free bonds are thought of as in the same plane, with the plane of the double bond perpendicular to that of the free bonds.

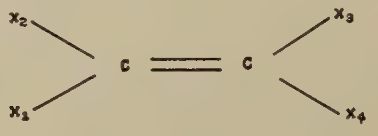


Figure 10

The figure supply consists of the alkyl radicals and the hydrogen atom.

The group of permissible permutations, which allow superposition of the resulting configuration on the original, is

$$I = (1)(2)(3)(4),\ (12)(34),\ (13)(24),\ (14)(23).$$

The cyclic indicator is

$$\frac{f_1^4 + 3f_2^2}{4} .$$

Again, no variable for the hydrogens is needed, since an alkene with n carbons necessarily has 2n hydrogen atoms. Hence one may let

$$a(x) = \sum_{n=2}^{\infty} A_n x^n$$

represent the enumerative power series of the stereoisomeric alkenes, where n is the number of carbon atoms. The enumerative power series of the figure supply is s(x). We find

$$a(x) = x^2 \frac{s(x)^4 + 3s(x^2)^2}{4} . \tag{4}$$

The factor x^2 accounts for the two carbons in the skeletal framework.

C. Paraffines

In the three dimensional model of the paraffines, the skeletal framework is not at once obvious. If one choses a regular tetrahedron with carbon at the center and all four vertices available for attaching alkyl radicals and hydrogen atoms, there will be considerable duplication. Even such a simple paraffine as propane will be counted twice, once with two methyl groups and two hydrogens attached to the vertices, once with one ethyl group and three hydrogens.

The concepts of "centric" and "bicentric" paraffines prove useful in avoiding duplication. A centric paraffine contains one carbon attached to two or more alkyl radicals, each of which has less than n/2 carbons in it. A bicentric paraffine contains one single bond to which are attached two alkyl radicals, each one of which has n/2 carbons in it. All paraffines are of one type or the other. Bicentric paraffines can occur only if n is even.

The skeletal framework for the bicentric paraffines is the one single bond. It is not necessary to get a cyclic indicator for this type. On using T_n'' for the number of stereoisomeric bicentric paraffines with carbon content n, T_n' for the number of stereoisomeric centric paraffines, and T_n for the total number of stereoisomeric paraffines, one obtains

$$T_n'' = \frac{S_{n/2}\,(S_{n/2} + 1)}{2} , \tag{5}$$

the formula for the number of combinations, with repetitions allowed, of $S_{n/2}$ things taken two at a time. If n is odd, $T_n'' = 0$.

The skeletal framework for the centric paraffines is a regular tetrahedron, with carbon at the center, and the four vertices as available positions. The figure supply is limited to hydrogen atoms and alkyl radicals containing less than n/2 carbons.

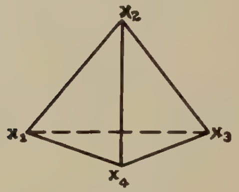


Figure 11

For the enumerative power series of the figure supply, one needs the notation

$$S_0 + S_1 x + S_2 x^2 + \cdots + S_N x^N = \overset{N}{s}(x).$$

The group of permissible permutations, which allow superposition of the resulting configuration on the original, is the alternating group on four numbers. Hence the cyclic indicator is

$$\frac{f_1^{\,4} + 3f_2^{\,2} + 8f_1 f_3}{12}.$$

Using the Pólya method, one finds

$$T_n' = \operatorname{coeff}_n \left\{ x \; \frac{\overset{N}{s}(x)^4 + 3\overset{N}{s}(x^2)^2 + 8\,\overset{N}{s}(x)\overset{N}{s}(x^3)}{12} \right\} \tag{6}$$

$$\frac{n}{2} - 1 \leqq N < \frac{n}{2}.$$

(By coeff_n is meant the coefficient of x^n in the expression given). The necessity of using the functional equation for but one term comes from the changing of figure supply with each increase in the number of carbon atoms in the molecules.

Finally,

$$T_n = T_n' + T_n''. \tag{7}$$

DETERMINATION OF FUNCTIONAL EQUATIONS FOR ENUMERATION OF ENANTIOMORPHS AND NON-ENANTIOMORPHS

Since the stereoisomers can be divided into two classes, the enantiomorphic and the non-enantiomorphic, it is possible to use indirect enumeration. Having obtained the enumerative power series for all the stereoisomers, it suffices to obtain that for the non-enantiomorphs, and to obtain the series for the enantiomorphs by subtraction.

A. Alcohols

There are three types of structure which the model of a non-enantiomorphic alcohol can have.

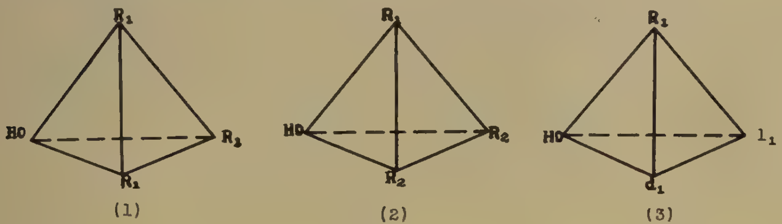


Figure 12

(Here R_i, d_j, and l_j represent alkyl redicals, R_i meaning nonenantiomorphic radicals, or hydrogens, and d_j and l_j enantiomorphic ones.) No other alcohols have models which are superimposable on their mirror images.

Interchanging the d_1 and l_1 in (3) gives a different molecule, although one of the same type. Hence, using the skeletal framework

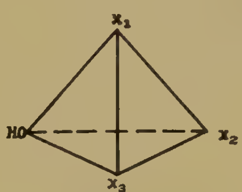


Figure 13

one may obtain a distinct non-enantiomorphic alcohol by attaching to x_1 any non-enantiomorphic alkyl radical or hydrogen, attaching to x_2 any alkyl radical or a hydrogen, and attaching to x_3 the mirror image of the figure attached to x_2.

Such a skeletal framework is abstractly identical with the three positions,

$$\overset{\bullet}{y_1} \qquad \overset{\bullet}{z_1} \qquad \overset{\bullet}{w_1},$$

where y_1 corresponds to the center of the tetrahedron, z_1 to the vertex x_1, and w_1 to the pair of vertices x_2 and x_3. The figure supply for y_1 is one carbon atom, for z_1 of the non-enantiomorphic alkyl radicals (or a hydrogen atom), and that for w_1 consists of a pair of alkyl radicals (or a pair of hydrogens). The figure attached to x_1 is the mirror image of that attached to x_3. Since the figure supply for each abstract position is independent of that for the others, it is a case of the direct product. The group for each position is the identity I. Hence, the cyclic indicator for y_1 is f_1, the cyclic indicator of z_1 is g_1, and the cyclic indicator for w_1 is h_1. Consequently the cyclic indicator for the direct product I x I x I is

$$f_1\, g_1\, h_1.$$

Letting $i(x) = \sum_{n=0}^{\infty} I_n x^n$ be the enumerative power series for the non-enantiomorphic alcohols ($I_0 = S_0 = 1$), and recalling that the enumerative power series for the non-enantiomorphic alkyl radicals is the same, we have

$$i(x) = 1 + x\, i(x) s(x^2). \tag{8}$$

The 1 is added to take care of the case HOH, counted as an alcohol of zero carbon content.

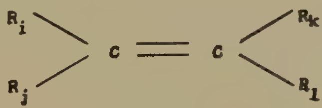
Letting $m(x) = \sum_{n=0}^{\infty} M_n x^n$ be the enumerative power series for the enantiomorphic alcohols, one has

$$m(x) = s(x) - i(x). \tag{9}$$

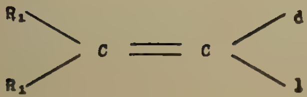
Because enantiomorphs always come in pairs, the coefficients of $m(x)$ are always even.

B. Alkenes

The following are the thirteen types of structure available for models of non-enantiomorphic alkenes:



(1)



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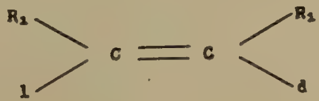

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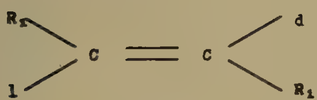

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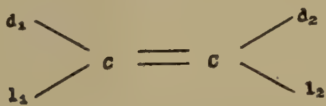

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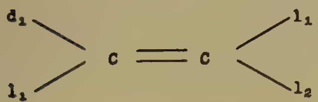

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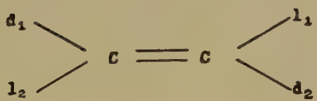

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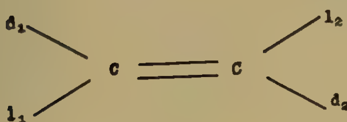

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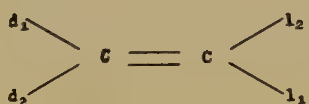

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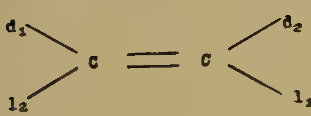

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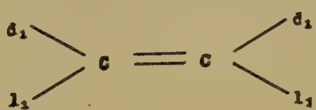

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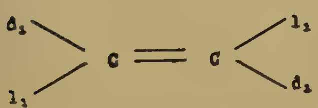


(12)

(13)

(Again the attached figures represent alkyl radicals or hydrogens.) All other alkenes have models which are not superimposable on their mirror images.

Type (1) has the same skeletal framework as the stereoisomeric alkenes (Figure 10), but its figure supply consists of the non-enantiomorphic alkyl radicals. Hence its functional equation is

$$b_1(x) = x^2 \, \frac{i(x)^4 + 3i(x^2)^2}{4} .$$

Types (2), (3), and (4) give distinct molecules, but each has a skeletal framework abstractly identical with the three positions

$$\overset{\bullet}{y_1} \qquad \overset{\bullet}{z_1} \qquad \overset{\bullet}{w_1} \, ,$$

where y_1 corresponds to the double bond, z_1 corresponds to the pair of bonds with R_1's attached, and w_1 corresponds to the pair of bonds with d and l attached. The figure supply for y_1 is a pair of carbon atoms, that for z_1 consists of pairs of identical non-enantiomorphic alkyl radicals or hydrogen atoms, and that for w_1 of pairs of enantiomorphic alkyl radicals (one the mirror image of the other). The enumerative power series of enantiomorphic pairs of alkyl radicals is

$$\frac{m(x^2)}{2} .$$

Since the figure supply for each abstract position is independent of the other two, it is again a case of the direct product I x I x I, and the functional equation for enumerating types (2), (3), and (4) is

$$b_2(x) = 3 \, x^2 i(x^2) \, \frac{m(x^2)}{2} .$$

Types (5) to (13) can be accounted for by adding an extra set of types (11), (12), (13) and then subtracting it later. With the extra set, on using the combinations of types (5) and (11), (10) and (11), (6) and (13), (7) and (12), (8) and (12), (9) and (13), it is seen that, apart from the double bond, each of these combinations has a skeletal framework abstractly identical with

$$\underset{x_1}{\bullet}\!\!-\!\!-\!\!-\!\!-\!\!\underset{x_2}{\bullet}$$

providing one uses as figure supply pairs of enantiomorphic alkyl radicals. Here x_1 corresponds to the pair of bonds attached to d_1 and l_1, and x_2 corresponds to the pair of bonds attached to d_2 and l_2. The group of permissible permutations is $I = (1)(2), (12)$.

Consequently the cyclic indicator is

$$\frac{f_1^2 + f_2}{2},$$

and, for the six combinations, the functional equation is

$$b_3(x) = 6x^2 \frac{[m(x^2)/2)]^2 + m(x^4)/2}{2}.$$

(The factor x^2, as before, accounts for the two carbons of the double bond.)

The extra set of types (11), (12), (13) may be subtracted after abstractly identifying the skeletal framework of each of them with a single position x_1, and using the abstract figure supply of two identical pairs of enantiomorphic alkyl radicals. The only permissible permutation is the identity, so the cyclic indicator is f_1. The Pólya method yields, for these three types, the functional equation

$$b_4(x) = \frac{3x^2 m(x)^4}{2}.$$

Altogether, then, the number of non-enantiomorphic alkenes is given by

$$b(x) = b_1(x) + b_2(x) + b_3(x) - b_4(x),$$

or, combining terms,

(10) $$b(x) = \frac{x^2[\, i(x)^4 + 3\, s(x^2)^2]}{4}$$

$$\left[b(x) = \sum_{n=2}^{\infty} B_n x^n \right].$$

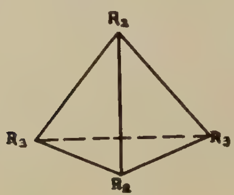
Letting $c(x) = \sum_{n=2}^{\infty} C_n x^n$ be the enumerative power series for the

enantiomorphic alkenes, one has

$$c(x) = a(x) - b(x). \tag{11}$$

C. Paraffines.

Models of non-enantiomorphic centric paraffines must be of one of the following types of structure:



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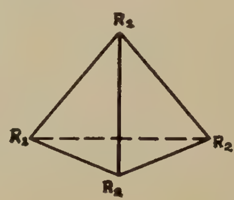

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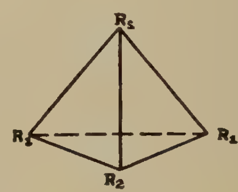

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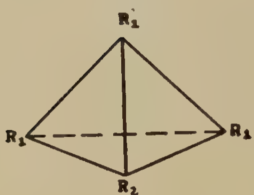

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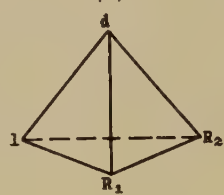

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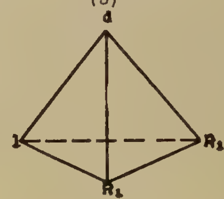

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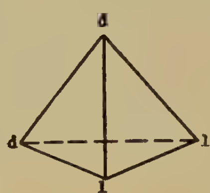


(7)

Types (1) to (4) can be accounted for if one considers three combinations which are defined as follows:

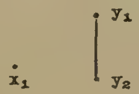
Combination α consists of type (1), two types (2), type (3), and type (4).

Combination β consists of type (2) and type (4).

Combination γ consists of type (4).

Types (1) to (4) are then equivalent to combination α plus combination γ minus combination β.

Combination α has a skeletal framework which, apart from the central carbon in the tetrahedron (not shown), is abstractly identical with



where the figure supply for x_1 consists of identical pairs of non-enantiomorphic alkyl radicals with carbon content less than n/2 (or hydrogens), and that for the y's consists of the non-enantiomorphic alkyl radicals with carbon content less than n/2 (or hydrogens). One sees that x_1 corresponds to the two vertices attached to R_1's in all four types, and that y_1 and y_2 correspond to the other two vertices. The permissible group on x_1 is the identity, and that on the y's is I = (1)(2), (12). The figure supplies are independent, so it is a case of the direct product, and the cyclic indicator for the abstract skeletal framework is

$$f_1 \; \frac{g_1^2 + g_2}{2}.$$

The enumerative power series of the abstract figure supplies are

$$f_1 = \overset{N}{i}(x^2) \quad \text{and } g_1 = \overset{N}{i}(x),$$

$$n/2 - 1 \leq N < n/2.$$

Hence the functional expression for combination α is

$$\mathrm{coeff}_n \left\{ x \;\; \overset{N}{i}(x^2) \;\; \frac{\overset{N}{i}(x)^2 + \overset{N}{i}(x^2)}{2} \right\}.$$

(The factor x takes care of the carbon atom in the center of the tetrahedron.)

Combination β has a skeletal framework which, apart from the center carbon, is abstractly identical with

$$\left|\begin{array}{l} x_1 \\ \\ x_2 \end{array}\right. ,$$

where the figure supply consists of identical pairs of non-enantiomorphic alkyl radicals with carbon content less than n/2 (or hydrogens). One sees that x_1 corresponds to the pair of vertices attached to R_1's in type (2), and that x_2 corresponds to the other pair of vertices. The permissible group is I = (1)(2), (12). The cyclic indicator for the abstract skeletal framework is

$$\frac{h_1^2 + h_2}{2} .$$

The enumerative power series of the abstract figure supply is

$$h_1 = \overset{N}{i}(x^2), \qquad \text{where } n/2 - 1 \leq N < n/2.$$

Hence the functional expression for combination β is

$$\operatorname{coeff}_n \left\{ x \; \frac{\overset{N}{i}(x^2)^2 + \overset{N}{i}(x^4)}{2} \right\} .$$

Combination γ has a skeletal framework which, apart from the center carbon, is abstractly identical with a single position x_1, corresponding to all four vertices, where the figure supply consists of four identical non-enantiomorphic alkyl radicals, each with carbon content less than n/2 (or hydrogens). The permissible group is the identity, so the cyclic indicator is simply k_1. The enumerative power series of the abstract figure supply is

$$k_1 = \overset{N}{i}(x^4), \qquad \text{where } n/2 - 1 \leq N < n/2.$$

Hence the functional expression for combination γ is

$$\operatorname{coeff}_n \left\{ x \, \overset{N}{i}(x^4) \right\} .$$

Types (1) to (4) then have the functional equation

$$J'_{1,n} = \operatorname{coeff}_n \left\{ x \; \frac{\overset{N}{i}(x^2) \, \overset{N}{i}(x)^2 + \overset{N}{i}(x^4)}{2} \right\} .$$

The combination of types (5) and (6) has a skeletal framework which, apart from the central carbon, is abstractly identical with

$$\cdot x_1 \qquad \begin{array}{l} \bullet\ y_1 \\ | \\ \bullet\ y_2 \end{array}$$

where the figure supply for x_1 consists of pairs of non-enantiomorphic alkyl radicals, each with carbon content less than n/2, and that for the y's consists of the nonenantiomorphic alkyl radicals with carbon content less than n/2 (or hydrogens). We see that x_1 corresponds to the pair of vertices in types (5) and (6),arrached to d and l, and that y_1 and y_2 correspond to the other two vertices. The permissible group on x_1 is I = (1), and the permissible group on the y's is I = (1)(2). The figure supplies are independent, so it is a case of the direct product, and the cyclic indicator for the abstract skeletal framework is

$$f_1\, g_1^{\,2}.$$

The enumerative power series of the abstract figure supplies are

$$f_1 = \frac{\overset{N}{m}(x^2)}{2}, \quad g_1 = \overset{N}{i}(x),$$

where $n/2 - 1 \leqq N < n/2$.

Hence the functional equation for types (5) and (6) is

$$J'_{2,n} = \text{coeff}_n \left\{ x \ \frac{\overset{N}{m}(x^2)\ \overset{N}{i}(x)^2}{2} \right\}.$$

Type (7) has a skeletal framework abstractly identical with a single position x_1, where the figure supply consists of two identical pairs of enantiomorphic alkyl radicals, each radical with carbon content less than n/2. The permissible group is I = (1), so the cyclic indicator for the abstract skeletal framework is f_1. The enumerative power series of the abstract figure supply is

$$f_1 = \frac{\overset{N}{m}(x^4)}{2}, \qquad \text{where } n/2 - 1 \leqq N < n/2.$$

Hence the functional equation for type (7) is

$$J'_{3,n} = \text{coeff}_n \left\{ x \; \frac{\overset{N}{m}(x^4)}{2} \right\} .$$

For all seven types, letting J'_n be the number of non-enantiomorphic centric paraffines of carbon content n, one obtains

$$J'_n = J'_{1,n} + J'_{2,n} + J'_{3,n} ,$$

or

$$J_n = \text{coeff}_n \left\{ x \; \frac{\overset{N}{i}(x)^2 \;\; S(x^2) + S(x^4)}{2} \right\} \tag{12}$$

where $n/2 - 1 \leq N < n/2$.

Models of the non-enantiomorphic bicentric paraffines must be of one of the following types of structure:

R_1•————•R_1	R_1•————•R_2	l•————•d
(1)	(2)	(3)

(In type (2), R_1 and R_2 are of the same carbon content.)

The bicentric paraffines do not require a cyclic indicator. Types (1) and (2) are accounted for by

$$J''_{1,n} = I_{n/2}(I_{n/2} + 1)/2 .$$

Type (3) is accounted for by

$$J''_{2,n} = \frac{M_{n/2}}{2} ,$$

the number of pairs of enantiomorphic alkyl radicals with carbon content n/2.

For all three types, letting J''_n represent the number of non-enantiomorphic bicentric paraffines with carbon content n, one obtains

$$J''_n = J''_{1,n} + J''_{2,n} ,$$

or

$$J''_n = \frac{[I_{n/2}]^2 + S_{n/2}}{2} . \tag{13}$$

Letting J_n represent the number of non-enantiomorphic paraffines and and N_n the number of enantiomorphic paraffines of carbon content n, one obtains the results

(14) $$J_n = J'_n + J''_n,$$

and

(15) $$N_n = T_n - J_n.$$

If one desires to obtain enumerative power series with the paraffines, it is only necessary to use J_n, N_n, and T_n as the coefficients of x^n in the various series.

ASYMPTOTIC BEHAVIOR OF COEFFICIENTS

Since it does not seem possible to obtain general expressions for the n^{th} coefficients in the power series determined by the functional equations, it is desirable to determine asymptotic expressions which enable one to approximate the coefficients as the value of n becomes large.

For this purpose, the following notation is useful:

$A_n \approx B_n$ (read "A_n is asymptotically proportional to B_n")

if

$$\lim_{n \to \infty} \frac{A_n}{B_n} = C, \qquad 0 < C < \infty.$$

$A_n \sim B_n$ (read "A_n is asymptotically equal to B_n")

if

$$\lim_{n \to \infty} \frac{A_n}{B_n} = 1.$$

$A_n = O[f(n)]$ (read "A_n is of the order of f(n)")

if, from some value of n on,

$$|A_n|/f(n)$$

is bounded.

A function F(x) is said to possess an algebraic singularity at the point c, if, in a sufficiently small neighborhood of c, it can be represented by a sum of a finite number of terms of the form

$$(x - c)^{-t}\,\phi(x),$$

where t designates any complex constant whatsoever different from

0, -1, -2, $\cdots$, and $\phi(x)$ is regular at c, $\phi(c) \neq 0$, Each term is said to have a singularity of <u>weight</u> $\mathcal{R}(t)$ (real part of t). If there is a single term of greatest weight $\mathcal{R}(t_1)$, the function is said to have a singularity of weight $\mathcal{R}(t_1)$.

With some of the functions, their behavior in the neighborhood of the algebraic singularity of greatest weight on the circle of convergence being known, the following lemma is useful (12).

Lemma:

The power series with integral coefficients

$$f(x) = a_0 + a_1x + a_2x^2 + \cdots + a_nx^n + \cdots$$

shall have on its circle of convergence only a finite number of singular points, each of which is an algebraic singularity. Further, there shall be one singularity of greatest weight, in whose neighborhood the function represented has the form

$$f(x) = (1 - \frac{x}{\alpha})^{-s}\, G(x) + (\text{other terms of less weight}),$$

where α is real, where s is a real constant, not equal to a non-positive integer, and where G(x) signifies an analytic function which is regular in the neighborhood of $x = \alpha$; also, $G(\alpha) = A \neq 0$.
Then,

$$a_n \sim \alpha^{-n}\, n^{s-1}\, \frac{A}{\Gamma(s)}.$$

We are now in a position to proceed.

A. Alcohols

By comparison with other functional equations, Pólya has shown that s(x) has a radius of convergence σ, such that $0 < \sigma < 1$. Consequently, $s(x^3)$ has a radius of convergence $\sigma^{1/3} > \sigma$.

If one sets $y = s(x)$ and considers the functional equation (3) in the form

$$xy^3 - 3y + 2x\, s(x^3) + 3 = 0, \tag{16}$$

he see that $y = s(x)$ satisfies an equation of third degree whose coefficients

are regular inside the circle $|x| < \sigma^{1/3}$. With the analytic continuation of the element of the function $y = s(x)$, inside this circle, singularities can arise in only two ways. Either the coefficient of y^3 must vanish, or the equation must have a multiple root in y. The only place where the coefficient of y^3 vanishes is at $x = 0$, but here $y = s(x)$ is regular. Hence we are left with the second alternative.

Differentiating the left member of (16) partially with respect to y, and setting the result equal to zero, we have

$$xy^2 - 1 = 0. \tag{17}$$

Eliminating y between (16) and (17), we find that the equation

$$\frac{x\,[3 + 2x\,s(x^3)]^2}{4} = 1 \tag{18}$$

must be satisfied at the singular points.

Since $s(x)$ has purely positive coefficients, $x = \sigma$ is a singular point of $s(x)$, and $x = \sigma$ must satisfy (17) and (18). Further, the left member of (18) has purely non-negative coefficients. Then, along the circle of convergence, it attains its greatest absolute value at $x = \sigma$. Hence, equation (18) is satisfied only at $x = \sigma$ on the circle of convergence, so that $x = \sigma$ is the only singular point lying in the closed circle $|x| \leqq \sigma$.

Thus (17) becomes

$$\sigma\,[\,s(\sigma)]^2 = 1, \quad \text{or } s(\sigma) = \frac{1}{\sigma^{1/2}} \tag{19}$$

($s(x)$ is positive if x is positive).

Further, singular points can not have a cluster point inside the circle $|x| < \sigma^{1/3}$; so $x = \sigma$ can be neither a pole nor an essential singularity. It must, therefore, be a branch point.

To determine what kind of branch point it is, we proceed as follows:

We recall that $y = y_1 = s(x)$ is one solution of (16). After removing the factor $y - s(x)$ from (16), we are left with the quadratic in y,

$$xy^2 + xy\,s(x) + x\,s(x)^2 - 3 = 0. \tag{20}$$

Solution of (20) yields

(21) $$y_2 = \frac{-x\,s(x) + \sqrt{3[4x - x^2 s(x)^2]}}{2x},$$

(22) $$y_3 = \frac{-x\,s(x) - \sqrt{3[4x - x^2 s(x)^2]}}{2x}.$$

Setting $x = \sigma$, we get

$$y_1 = y_2 = \frac{1}{\sigma^{1/2}}, \quad y_3 = -\frac{2}{\sigma^{1/2}},$$

and we see that the branch point is one where two sheets of the Riemann surface are connected cyclically (a branch point of first order).

Hence, in the neighborhood of $x = \sigma$, $s(x)$ is developable in powers of $\sqrt{1 - \frac{x}{\sigma}}$, and the development begins

(23) $$s(x) = a - b\sqrt{1 - \frac{x}{\sigma}} + \cdots,$$

where

(24) $$a = s(\sigma) = \frac{1}{\sigma^{1/2}},$$

(25) $$b = \sqrt{\frac{s(\sigma) - 1 + 2\sigma^4 s'(\sigma^3)}{\sigma\, s(\sigma)}}.$$

The values of a and b are obtained as follows:

Recall

$$s(x) = a - b\sqrt{1 - \frac{x}{\sigma}} + \cdots$$

in the neighborhood of $x = \sigma$.

Let

$$t = \sqrt{1 - \frac{x}{\sigma}},$$

so that

$$x = \sigma(1 - t^2).$$

Then

$$s(x) = \Sigma(t) = a - bt + \cdots = \Sigma,$$

$$s(x^3) = \Sigma_3(t) = s\left\{[\sigma(1 - t^2)]^3\right\} = \Sigma_3,$$

where Σ and Σ_3 are analytic in the neighborhood of $t = 0$. Hence

$$\Sigma(t) = \Sigma(0) + \Sigma'(0)t + \cdots,$$

where

$$\Sigma(0) = s(\sigma) = a,$$

$$\Sigma'(0) = -b.$$

We may then write

$$\sigma(1-t^2)\Sigma^3 - 3\Sigma + 2\sigma(1-t^2)\Sigma_3 + 3 = 0.$$

Differentiating this with respect to t and solving for $\Sigma'(t)$,

$$\Sigma'(t) = \frac{-2\sigma(1-t^2)\Sigma'_3 + 2\sigma t(\Sigma^3 + 2\Sigma_3)}{3[\sigma(1-t^2)\Sigma^2 - 1]}.$$

Recalling

$$\sigma s(\sigma)^2 = 1,$$

we see that the denominator vanishes when t = 0. Further, in the neighborhood of t = 0,

$$\Sigma'_3 = -6t(1-t^2)\sigma^3 [s'(\sigma^3) + \cdots].$$

Hence

$$\Sigma'(0) = \frac{0}{0} \quad \text{(indeterminate)}.$$

But the coefficient of t in the denominator does not vanish, and we can still solve for b.

Since

$$\sigma(1-t^2)[\Sigma^3 + 2\Sigma_3] = 3[\Sigma - 1],$$

$$\Sigma^3 + 2\Sigma_3 = \frac{3[\Sigma - 1]}{\sigma}(1 + t^2 + t^4 + \cdots).$$

Therefore,

$$\Sigma'(t) = \frac{-2\sigma(1-t^2)[-6t(1-t^2)\sigma^3\{s'(\sigma^3) + \cdots\}] + 6t\{a-1 + \cdots\}\{1+t^2+\cdots\}}{3[\sigma(1-t^2)(a^2-2abt + \cdots) - 1]},$$

$$\Sigma'(0) = -b = \frac{12\sigma^4 s'(\sigma^3) + 6(a-1)}{-6\sigma ab},$$

and

$$b = \sqrt{\frac{s(\sigma) - 1 + 2\sigma^4 s'(\sigma^3)}{\sigma s(\sigma)}}.$$

By use of the lemma, we obtain

$$S_n \sim \sigma^{-n} n^{-3/2} \frac{b}{2\sqrt{\pi}} . \tag{26}$$

One may write (8) in the form

$$i(x) = \frac{1}{1 - x\, s(x^2)} . \tag{27}$$

The denominator on the right vanishes if $x = \sigma^{1/2}$, for, according to (19), $s(\sigma) = \frac{1}{\sigma^{1/2}}$; $i(-\sigma^{1/2}) = 1/2$. Because $s(x)$ has purely positive coefficients, $|x\, s(x^2)| < 1$ when $|x| \leq \sigma^{1/2}$ and $x \neq \pm\sigma^{1/2}$. Further, $i(x)$ is regular if $|x| < \sigma^{1/2}$, so that the radius of convergence of $i(x)$ is $\sigma^{1/2}$.

In order to determine the nature of the singularity of $i(x)$ at $x = \sigma^{1/2}$, we write, from (23),

$$s(x) = \sum_{n=0}^{\infty} a_n \left(1 - \frac{x}{\sigma}\right)^{n/2} , \tag{28}$$

where $a_0 = s(\sigma)$, $a_1 = -b$.

Therefore,

$$s(x) = \left(1 - \frac{x}{\sigma}\right)^{1/2} \left[a_1 + a_3\left(1 - \frac{x}{\sigma}\right) + a_5\left(1 - \frac{x}{\sigma}\right)^2 + \cdots\right]$$

$$+ \left[s(\sigma) + a_2\left(1 - \frac{x}{\sigma}\right) + a_4\left(1 - \frac{x}{\sigma}\right)^2 + \cdots\right],$$

or

$$s(x) = \left(1 - \frac{x}{\sigma}\right)^{1/2} F_1(x) + G_1(x), \tag{29}$$

where $F_1(x)$ and $G_1(x)$ are regular at $x = \sigma$, $F_1(\sigma) = -b$, and $G_1(\sigma) = s(\sigma)$.

Hence,

$$s(x^2) = \left(1 - \frac{x^2}{\sigma}\right)^{1/2} F_1(x^2) + G_1(x^2)$$

$$= \left(1 - \frac{x}{\sigma^{1/2}}\right)^{1/2} \left[\left(1 + \frac{x}{\sigma^{1/2}}\right)^{1/2} F_1(x^2)\right] + G_1(x^2),$$

or

$$s(x^2) = \left(1 - \frac{x}{\sigma^{1/2}}\right)^{1/2} F_2(x) + G_2(x), \tag{30}$$

where $F_2(x)$ and $G_2(x)$ are regular at $x = \sigma^{1/2}$, $F_2(\sigma^{1/2}) = -\sqrt{2}b$, and $G_2(\sigma^{1/2}) = s(\sigma)$.

Then,

$$1 - x\, s(x^2) = \left(1 - \frac{x}{\sigma^{1/2}}\right)^{1/2} (-x\, F_2(x)) + (1 - x\, G_2(x)),$$

or

$$1 - x\,s(x^2) = \left(1 - \frac{x}{\sigma^{1/2}}\right)^{1/2} F_3(x) + G_3(x), \tag{31}$$

where $F_3(x)$ and $G_3(x)$ are regular at $x = \sigma^{1/2}$, $F_3(\sigma^{1/2}) = \sqrt{2\sigma}\,b$, $G_3(\sigma^{1/2}) = 0$.

Further,

$$G_3(x) = \left(1 - \frac{x}{\sigma^{1/2}}\right) H(x)$$

where $H(x)$ is regular at $x = \sigma^{1/2}$.

Hence,

$$i(x) = \frac{1}{1 - x\,s(x^2)} = \frac{1}{\left(1 - \frac{x}{\sigma^{1/2}}\right)^{1/2} F_3(x) + G_3(x)} .$$

Then

$$i(x) = \frac{1}{\left(1 - \frac{x}{\sigma^{1/2}}\right)^{1/2} F_3(x) + G_3(x)} \quad \frac{\left(1 - \frac{x}{\sigma^{1/2}}\right)^{1/2} F_3(x) - G_3(x)}{\left(1 - \frac{x}{\sigma^{1/2}}\right)^{1/2} F_3(x) - G_3(x)}$$

$$= \frac{\left(1 - \frac{x}{\sigma^{1/2}}\right)^{1/2} F_3(x)}{\left(1 - \frac{x}{\sigma^{1/2}}\right) F_3(x)^2 - G_3(x)^2} - \frac{G_3(x)}{\left(1 - \frac{x}{\sigma^{1/2}}\right) F_3(x)^2 - G_3(x)^2}$$

$$= \frac{\left(1 - \frac{x}{\sigma^{1/2}}\right)^{1/2} F_3(x)}{\left(1 - \frac{x}{\sigma^{1/2}}\right)\left[F_3(x)^2 - \left(1 - \frac{x}{\sigma^{1/2}}\right) H(x)^2\right]} - \frac{\left(1 - \frac{x}{\sigma^{1/2}}\right) H(x)}{\left(1 - \frac{x}{\sigma^{1/2}}\right)\left[F_3(x)^2 - \left(1 - \frac{x}{\sigma^{1/2}}\right) H(x)^2\right]}$$

$$= \left(1 - \frac{x}{\sigma^{1/2}}\right)^{-1/2} \quad \frac{F_3(x)}{F_3(x)^2 - \left(1 - \frac{x}{\sigma^{1/2}}\right) H(x)^2} - \frac{H(x)}{F_3(x)^2 - \left(1 - \frac{x}{\sigma^{1/2}}\right) H(x)^2} ,$$

or

$$i(x) = \left(1 - \frac{x}{\sigma^{1/2}}\right)^{-1/2} F_4(x) + G_4(x), \tag{32}$$

where $F_4(x)$ and $G_4(x)$ are regular at $x = \sigma^{1/2}$, $F_4(\sigma^{1/2}) = \frac{1}{\sqrt{2\sigma}\,b}$.

Similar treatment applied to $i(x)$ at $x = -\sigma^{1/2}$, the only other singular point on the circle of convergence, shows that in the neighborhood of $x = -\sigma^{1/2}$,

$$i(x) = \left(1 + \frac{x}{\sigma^{1/2}}\right)^{1/2} F_5(x) + G_5(x)$$

where

$$F_5(x) \text{ and } G_5(x) \text{ are regular, } F_5(-\sigma^{1/2}) \neq 0.$$

Hence the singularity of greatest weight is at $x = \sigma^{1/2}$, and, on using the lemma, we obtain

$$I_n \sim \sigma^{-n/2} n^{-1/2} \frac{1}{\sqrt{2\pi\sigma}\, b}. \tag{33}$$

From (9), $M_n = S_n - I_n$; by comparison of (26) with (30), we see that S_n is of higher order than I_n.

Hence,

$$M_n \sim S_n. \tag{34}$$

B. Alkenes.

From (4) we see that we may consider $a(x)$ as a function, $F(x, s(x), s(x^3))$, which has no singular points, other than $x = \sigma$, in the circle $|x| \leqq \sigma$.

Further, in the neighborhood of $x = \sigma$, $s(x)$ is the only argument which is irregular, and $s(x)$ has but a branch point of first order there.

Hence, in the neighborhood of $x = \sigma$, $a(x)$ is expansible in powers of $\sqrt{1 - \frac{x}{\sigma}}$, and begins

$$F(\sigma, s(\sigma), s(\sigma^3)) - \left\{\partial F/\partial[s(x)]\right\}_{x=\sigma} b \sqrt{1 - \frac{x}{\sigma}} + \cdots,$$

or

$$a(x) = a(\sigma) - \sigma^2 s(\sigma)^3 b \sqrt{1 - \frac{x}{\sigma}} + \cdots, \tag{35}$$

Using the lemma, and recalling $s(\sigma) = \frac{1}{\sigma^{1/2}}$, we find

$$A_n \sim \sigma^{-n} n^{-3/2} \frac{b\,\sigma^{1/2}}{2\sqrt{\pi}}. \tag{36}$$

It is convenient to think of (10) as

$$b(x) = b'(x) + b''(x), \tag{37}$$

where

$$b'(x) = \frac{x^2 i(x)^4}{4}, \tag{38}$$

(39) $$b''(x) = \frac{3x^2 s(x^2)^2}{4}.$$

It is desirable to discuss (38) and (39) separately, as each has the radius of convergence $\sigma^{1/2}$, and each has its important singularity at $x = \sigma^{1/2}$.

From (32)

(40) $$b'(x) = \left(1 - \frac{x}{\sigma^{1/2}}\right)^{-2} \frac{x^2 F_4(x)^4}{4} + \text{(terms of less weight)},$$

where $F_4(x)^4$ is regular at $x = \sigma^{1/2}$, $F_4(\sigma^{1/2})^4 = \frac{1}{4\sigma^2 b^4}$, and the other terms have asymptotic values of lower order in n.

Hence, using the lemma,

(41) $$B'_n \sim \sigma^{-n/2}\, n\, \frac{1}{16\sigma b^4}.$$

From (30)

$$b''(x) = \left(1 - \frac{x}{\sigma^{1/2}}\right)^{1/2} (2F_2(x)G_2(x))\left(\frac{3x^2}{4}\right) + \frac{3x^2}{4}\left[\left(1 - \frac{x}{\sigma^{1/2}}\right)F_2(x)^2 + G_2(x)^2\right],$$

or

(42) $$b''(x) = \left(1 - \frac{x}{\sigma^{1/2}}\right)^{1/2} D(x) + E(x),$$

where $D(x)$ and $E(x)$ are regular at $x = \sigma^{1/2}$, and $D(\sigma^{1/2}) = \frac{-3\sqrt{2\sigma}\, b}{2}$.

Consequently, the asymptotic value of B''_n is of lower order than that of B'_n, so

$$B_n \sim B'_n,$$

or

(43) $$B_n \sim \sigma^{-n/2}\, n\, \frac{1}{16\sigma b^4}.$$

From (11),

(44) $$C_n = A_n - B_n.$$

Comparing (36) and (43), we see that A_n is of higher order than B_n, so

$$C_n \sim A_n$$

or

$$C_n \sim \sigma^{-n} n^{-3/2} \frac{b\sigma^{1/2}}{2\sqrt{\pi}} . \tag{45}$$

C. Paraffines

From (5), we see that

$$T''_n \sim \frac{(S_{n/2})^2}{2}, \tag{46}$$

and, by (26),

$$T''_n \sim \sigma^{-n} n^{-3} \frac{b^2}{\pi} . \tag{47}$$

One may write (6) in the form

$$T'_n = \frac{1}{12} W_n + \frac{1}{4} Y_n + \frac{2}{3} Z_n, \tag{48}$$

where

$$W_n = \Sigma\ S_i S_j S_k S_l \qquad (i + j + k + l = n - 1), \tag{49}$$

$$Y_n = \Sigma\ S_i S_j \qquad (2i + 2j = n - 1), \tag{50}$$

$$Z_n = \Sigma\ S_i S_j \qquad (i + 3_j = n - 1). \tag{51}$$

The summations are over the integral solutions of the equations in parentheses, subject to the further restrictions,

$$0 \leqq i < n/2, \quad 0 \leqq j < n/2, \quad 0 \leqq k < n/2, \quad 0 \leqq l < n/2.$$

If there are no integral solutions in a particular case, the coefficient for that value of n is to be interpreted as zero. (E.g. If n is even, $Y_n = 0$).

In order to obtain asymptotic expressions for W_n, Y_n, and Z_n, it is important to establish several results.

On referring to (26), one sees that there exists a positive number C such that

$$S_m \sigma^m m^{3/2} < C \qquad \text{for } m = 1,2,3, \cdots , \tag{52}$$

Hence, considering

$$\sum_{k=0}^{\infty} (2k+1)\ S_k^2 \sigma^{2k} , \tag{53}$$

it is seen that

$$\sum_{k=1}^{\infty} (2k+1)s_k^{2}\sigma^{2k} < C^2 \sum_{k=1}^{\infty} \frac{2k+1}{k^3} < 3C^2 \sum_{k=1}^{\infty} \frac{1}{k^2},$$

so (53) converges. Further

(54) $$s_0 + s_1\sigma + \dots + s_k\sigma^k + \dots = s(\sigma) = \frac{1}{\sigma^{1/2}}.$$

We need to establish a result concerning μ, whose definition follows. Consider the solutions of the equation

(55) $$i + j + 2k = n - 1,$$

subject to the restriction that i, j, k are integers,

(56) $$0 \leqq i < n/2, \quad 0 \leqq j < n/2, \quad 0 \leqq k < n/2.$$

If we restrict k further by requiring

(57) $$0 \leqq k \leqq \frac{n-3}{6},$$

then it is impossible that either i or j become zero. In this case, to each value of k corresponds a value of μ, defined to be the smaller of the numbers i and j. Because of (55), (56), and (57),

(58) $$\mu > n/6.$$

For a fixed value of k, L(k) shall be defined as the number of pairs of values i, j which satisfy (56) as well as (55). If we write (55), according as n is even or odd,

$$(n/2 - i) + (n/2 - j) = 2k+1, \quad \left(\frac{n+1}{2} - i\right) + \left(\frac{n-1}{2} - j\right) = 2k+1,$$

one can easily establish that

(59) $$L(k) \leqq 2k + 1.$$

From (50), we can write

(60) $$Y_n = \sigma^{-n}\sigma\left[\sigma^{\frac{n-1}{3}} \sum s_i\sigma^i s_j\sigma^j \sigma^{\left\{2j - \frac{n-1}{3}\right\}}\right].$$

But

$$\sum s_i\sigma^i s_j\sigma^j \leq \sum s_i\sigma^i \sum s_j\sigma^j = \frac{1}{\sigma},$$

and $0 < \sigma < 1$, so

(61) $$\sigma^{n}Y_n \longrightarrow 0.$$

From (51) we can write

(62) $$Z_n = \sigma^{-n}\sigma\left[\sigma^{\frac{n-1}{3}} \sum s_i\sigma^i s_j\sigma^j \sigma^{\left\{2j - \frac{n-1}{3}\right\}}\right].$$

Since

$$i + 3j = n - 1,$$
$$3j = n - 1 - i \geq \frac{n-1}{2}$$

Hence

$$2j \geq \frac{n-1}{3},$$

so $\sigma^{\left\{2j - \frac{n-1}{3}\right\}}$ will always be a non-negative power of σ.

Therefore,

(63) $$\sigma^{n} Z_n \longrightarrow 0.$$

In order to evaluate W_n, we write

(64) $$W_n = W_n' + W_n'' + W_n''' .$$

W_n''' includes just those terms of the sum, in which all four summation indices i, j, k, l are greater than $\frac{n-3}{6}$.

W_n'' includes the terms of the sum, in which the two smallest indices i, j, k, l are equal to one another and both $\leq \frac{n-3}{6}$.

W_n' includes, consequently, those terms of the sum in which the minimum of i, j, k, l is reached by only one of these numbers and is $\leq \frac{n-3}{6}$.

(It is impossible for more than two indices to be less than or equal to $\frac{n-3}{6}$, under the restriction that each index be less than $n/2$.)

The entire sum in (49) contains less than n^3 terms.

Consider

(65) $$\sigma^{n}W_n = \sigma\left[\sum s_i\sigma^i s_j\sigma^j s_k\sigma^k s_l\sigma^l\right].$$

In those terms which belong to $W_n''' \sigma^n$, <u>each factor</u> of the summand, by virtue of (52), is

$$O(n^{-3/2}).$$

Hence

(66) $$\sigma^n W_n''' = O(n^{-12/2} \cdot n^3) = O(n^{-3}).$$

That part of $\sigma^n W_n''$ which arises from the terms with $k = 1$ is not greater than

$$\sigma \sum_{k=0}^{\frac{n-3}{6}} S_k^2 \sigma^{2k} \sum_{i,j} S_i \sigma^i S_j \sigma^j$$

$$< \sigma \sum_{k=0}^{\frac{n-3}{6}} S_k^2 \sigma^{2k} C^2 \mu^{-3} L(k)$$

$$< n^{-3} C^2 6^3 \sum_{k=0}^{\frac{n-3}{6}} (2k+1) S_k^2 \sigma^{2k} = O(n^{-3}).$$

Hence

(67) $$\sigma^n W_n'' = O(n^{-3}).$$

We separate the terms out of the sum W_n' into four categories, according as i, j, k, or l is the smallest of these four numbers. The terms in each category have equal sums; therefore, picking out l,

(68) $$\sigma^n W_n' = 4 \sum_{l=0}^{\frac{n-3}{6}} S_l \sigma^l W_{n,l} ,$$

where

(69) $$W_{n,l} = \sigma \sum_{i,j,k} S_i \sigma^i S_j \sigma^j S_k \sigma^k$$

$$= \sigma n^{5/2} \sum_{i,j,k} S_i \sigma^i i^{3/2} S_j \sigma^j j^{3/2} S_k \sigma^k k^{3/2} \left(\frac{i}{n} \frac{j}{n} \frac{k}{n}\right)^{-3/2} \frac{1}{n^2} ;$$

the summation is to be extended over such triples (i,j,k) of whole numbers as have

$$i + j + k = n - 1 - l,$$

$$l < i < n/2, \quad l < j < n/2, \quad l < k < n/2.$$

With reference to (26), one sees from the appearance of (69) that, with a fixed l, as $n \to \infty$,

$$(70) \qquad n^{5/2} W_{n,1} \sim \left(\frac{b}{2\sqrt{\pi}}\right)^3 \sigma \sum_{i,j,k} \left(\frac{i}{n}\frac{j}{n}\frac{k}{n}\right)^{-3/2} \frac{1}{n^2}$$

$$\rightarrow \left(\frac{b}{2\sqrt{\pi}}\right)^3 \sigma \iint_D \left[xy(1-x-y)\right]^{-3/2} dx\, dy$$

$$= \left(\frac{b}{2\sqrt{\pi}}\right)^3 \sigma\, I.$$

The triangular region of integration, D, is given by

$$(71) \qquad x \leqq 1/2, \quad y \leqq 1/2, \quad x + y \geqq 1/2.$$

Out of (68) and (70), with reference to (54), it follows that

$$(72) \qquad \lim_{n\to\infty} n^{5/2} \sigma^{n} W_n' = 4\left(\frac{b}{2\sqrt{\pi}}\right)^3 \sigma\, I \sum_{l=0}^{\infty} s_l \sigma^l$$

$$= 4\sigma^{1/2} \left(\frac{b}{2\sqrt{\pi}}\right)^3 I.$$

Evaluation of the integral in (70) yields

$$(73) \qquad I = 12\pi.$$

Therefore,

$$(74) \qquad n^{5/2} \sigma^{n} W_n' \sim \frac{6\sigma^{1/2} b^3}{\sqrt{\pi}} .$$

On comparing (7), (47), (48), (61), (63), (64), (66), (67), and (74), we may write

$$(75) \qquad T_n \sim \frac{W_n'}{12} \sim \sigma^{-n} n^{-5/2} \frac{\sigma^{1/2} b^3}{2\sqrt{\pi}} .$$

Recalling (13), (26), and (33), we have

$$(76) \qquad \sigma^{n/2} J_n'' \sim n^{-1} \frac{1}{2\pi\sigma b^2} = O(n^{-1}).$$

One may write (12) in the form

$$(77) \qquad J_n' = 1/2\, U_n + 1/2\, V_n,$$

where

$$(78) \qquad U_n = \sum I_i I_j S_k \qquad (i + j + 2k = n - 1),$$

$$(79) \qquad V_n = S_i \qquad (4i = n - 1).$$

Again summation is over integral solutions of the equations in parentheses, subject to the further restrictions,

$$0 \leq i < n/2, \quad 0 \leq j < n/2, \quad 0 \leq k < n/2.$$

If i is an integer,

$$(80) \qquad \sigma^{n/2} V_n \sim \sigma^{n/4}(n-1)^{-3/2} \frac{4b\,\sigma^{1/4}}{\sqrt{\pi}} = O(\sigma^{n/4}[n-1]^{-3/2}).$$

Otherwise $V_n = 0$.

Consider

$$(81) \qquad n^{1/2}\sigma^{n/2}U_n = \sigma^{1/2}\Big[\sum_{i,j,k} I_i\sigma^{i/2}i^{1/2}I_j\sigma^{j/2}j^{1/2}S_k\sigma^{k}k^{3/2}\Big(\frac{i}{n}\,\frac{j}{n}\,\frac{k^3}{n^3}\Big)^{-1/2}\frac{1}{n^2}\Big].$$

From (26) and (33), we know that, given an $\varepsilon > 0$, there exists a finite n_1, such that the following is true:

If $n \geq n_1$,

$$\Big| I_n\sigma^{n/2}n^{1/2} - \frac{1}{\sqrt{2\pi\sigma}\,b}\Big| < \varepsilon\,\frac{1}{\sqrt{2\pi\sigma}\,b},$$

$$\Big| S_n\sigma^{n}n^{3/2} - \frac{b}{2\sqrt{\pi}}\Big| < \varepsilon\,\frac{b}{2\sqrt{\pi}}.$$

Further, we know that a positive constant C_1 exists, such that, for $n = 0,1,2, \cdots,$

$$I_n\sigma^{n/2}n^{1/2} < C_1,$$

$$S_n\sigma^{n}\,n^{3/2} < C_1.$$

With a given ε, each term in the brackets in (81) belongs to at least one of the following four sets:

Z_n' consists of those terms in which i, j, and k are greater than or equal to n_1.

Z_n'' consists of those terms in which $i < n_1$.

Z_n''' consists of those terms in which $j < n_1$.

Z^{iv} consists of those terms in which $k < n_1$.

Then, $n^{1/2}\sigma^{n/2}\,U_n$ will not be greater than

$$\sigma^{1/2}(Z_n' + Z_n'' + Z_n''' + Z_n^{iv}).$$

$$Z_n^{iv} < C_1^3 \sum_{i,j,k} \left(\frac{i}{n}\frac{j}{n}\frac{k^3}{n^3}\right)^{-1/2} \frac{1}{n^2},$$

where $0 \leqq k \leqq n_1$.

$$Z_n''' < C_1^3 \sum_{i,j,k} \left(\frac{i}{n}\frac{j}{n}\frac{k^3}{n^3}\right)^{-1/2} \frac{1}{n^2}.$$

where $0 \leqq j < n_1$.

$$Z_n'' < C_1^3 \sum_{i,j,k} \left(\frac{i}{n}\frac{j}{n}\frac{k^3}{n^3}\right)^{-1/2} \frac{1}{n^2},$$

where $0 \leqq i < n_1$.

$$Z_n' \sim \left(\frac{1}{\sqrt{2\pi\sigma}\, b}\right)^2 \left(\frac{b}{2\sqrt{\pi}}\right) \sum_{i,j,k} \left(\frac{i}{n}\frac{j}{n}\frac{k^3}{n^3}\right)^{-1/2} \frac{1}{n^2},$$

where

$$n_1 \leqq \begin{Bmatrix} i \\ j \\ k \end{Bmatrix} < n/2.$$

If one calls

$$x_i = \frac{i}{n}, \qquad y_j = \frac{j}{n}, \qquad z_k = \frac{k}{n},$$

and recalls that

$$i + j + 2k = n - 1,$$

he sees that each of the triple sums, as $n \longrightarrow \infty$, can be replaced by a double integral.

The area over which one integrates, in the case of Z_n', is either a square or a parallelogram, depending on the choice of variables of integration.

In the other three cases the areas vanish, and the contributions of Z_n'', Z_n''', Z_n^{iv} may be neglected.

Thus,

$$(82) \quad n^{1/2}\sigma^{-n/2}\, U_n \sim \sigma^{1/2} \left(\frac{1}{\sqrt{2\pi\sigma}\, b}\right)^2 \left(\frac{b}{2\sqrt{\pi}}\right) \sum_{i,j,k} \left(\frac{i}{n}\frac{j}{n}\frac{k^3}{n^3}\right)^{-1/2} \frac{1}{n^2},$$

where

$$n_1 \leqq \begin{Bmatrix} i \\ j \\ k \end{Bmatrix} < n/2.$$

If we choose to integrate with respect to x and y, the triple sum in (82) must be replaced by

$$\frac{1}{2} \int_0^{1/2} \int_0^{1/2} x^{-1/2} y^{-1/2} \left(\frac{1-x-y}{2}\right)^{-3/2} dxdy. \tag{83}$$

The 1/2 to the left can be accounted for as follows: In going from the double sum

$$\sum_{i,j} F(x_i, y_j) \, \Delta x \, \Delta y$$

to the double integral

$$\iint F(x,y) dx\, dy,$$

one needs to sum over all pairs of i and j.

In our case, because of the restriction

$$i + j = n - 2k - 1,$$

we see that when n - 2k - 1 is even, i and j must be both odd or both even; when n - 2k - 1 is odd, i and j can not be both odd or both even. Hence we are summing over only half of the possible pairs.

From (82) and (83) we see that

$$n^{1/2} \sigma^{n/2} U_n \sim \frac{1}{2\pi b \sqrt{2\pi\sigma}} \quad I', \tag{84}$$

where

$$I' = \int_0^{1/2} \int_0^{1/2} x^{-1/2} y^{-1/2} (1 - x - y)^{-3/2} dx\, dy.$$

Evaluation of this integral yields

$$I' = 2\pi. \tag{85}$$

Therefore

$$n^{1/2} \sigma^{n/2} U_n \sim \frac{1}{\sqrt{2\pi\sigma}\; b} \,. \tag{86}$$

On comparing (14), (76), (77), (80), and (86), we may write

(87) $$J_n \sim \frac{U_n}{2} \sim \frac{1}{2b\sqrt{2\pi\sigma}} \sigma^{-n/2} n^{-1/2} \sim \frac{I_n}{2}.$$

Finally, from (15), (75), and (87), we may write

(88) $$N_n \sim T_n.$$

NUMERICAL RESULTS FROM FUNCTIONAL EQUATIONS

Using the functional equations the author has obtained the results tabulated in the following pages. Definitions of the quantities tabulated below follow:

n: The number of carbon atoms in the molecule, referred to as "Carbon content" for brevity.

S_n: Steroisomeric alcohols

I_n: Non-enantiomorphic alcholls

M_n: Enantiomorphic alcohols

A_n: Stereoisomeric alkenes

B_n: Non-enantiomorphic alkenes

C_n: Enantiomorphic alkenes

J_n': Non-enantiomorphic centric paraffines

J_n'': Non-enantiomorphic bicentric paraffines

T_n': Stereoisomeric centric paraffines

T_n'': Stereoisomeric bicentric paraffines

J_n: Non-enantiomorphic paraffines

T_n: Stereoisomeric paraffines

N_n: Enantiomorphic paraffines

TABLE 1

n	S_n	I_n	M_n
0	1	1	0
1	1	1	0
2	1	1	0
3	2	2	0
4	5	3	2
5	11	5	6
6	28	8	20
7	74	14	60
8	199	23	176
9	551	41	510
10	1,553	69	1,484
11	4,436	122	4,314
12	12,832	208	12,624
13	37,496	370	37,126
14	110,500	636	109,864
15	328,092	1,134	326,958
16	980,491	1,963	978,528
17	2,946,889	3,505	2,943,384
18	8,901,891	6,099	8,895,792
19	27,012,286	10,908	27,001,378
20	83,300,275	19,059	82,281,216

TABLE 2

n	A_n	B_n	C_n
2	1	1	0
3	1	1	0
4	4	4	0
5	6	6	0
6	18	16	2
7	42	30	12
8	118	68	50
9	314	132	182
10	895	281	614
11	2,521	545	1,976
12	7,307	1,117	6,190
13	21,238	2,162	19,076
14	62,566	4,326	58,240
15	185,310	8,334	176,976
16	553,288	16,412	536,876
17	1,660,490	31,458	1,629,032
18	5,011,299	61,235	4,950,064
19	15,190,665	116,841	15,073,824
20	46,244,031	225,555	46,018,476

TABLE 3

n	J'_n	J''_n
1	1	0
2	0	1
3	1	0
4	1	1
5	3	0
6	2	3
7	7	0
8	7	7
9	21	0
10	22	18
11	61	0
12	72	46
13	186	0
14	220	135
15	567	0
16	717	364
17	1,755	0
18	2,209	1,116
19	5,454	0
20	7,149	3,157

TABLE 4

n	T'_n	T''_n
1	1	0
2	0	1
3	1	0
4	1	1
5	3	0
6	2	3
7	11	0
8	9	15
9	55	0
10	70	66
11	345	0
12	494	406
13	2,412	0
14	3,788	2,775
15	18,127	0
16	30,799	19,900
17	143,255	0
18	256,353	152,076
19	1,173,770	0
20	2,190,163	1,206,681

TABLE 5

n	J_n	T_n	N_n
1	1	1	0
2	1	1	0
3	1	1	0
4	2	2	0
5	3	3	0
6	5	5	0
7	7	11	4
8	14	24	10
9	21	55	34
10	40	136	96
11	61	345	284
12	118	900	782
13	186	2,412	2,226
14	355	6,563	6,208
15	567	18,127	17,560
16	1,081	50,699	49,618
17	1,755	143,255	141,500
18	3,325	408,429	405,104
19	5,454	1,173,770	1,168,316
20	10,306	3,396,844	3,386,538

ASYMPTOTIC EVALUATIONS

In order to make comparisons between the calculated values of the coefficients and the asymptotic approximations, it is necessary to approximate σ and b.

By comparing the functional equation for s(x) with

$$p(x) = 1 + x\, p(x)^3$$

$$\left(p(x) = \sum_{n=0}^{\infty} P_n x^n\right),$$

Pólya has shown that, for $n > 0$,

$$S_n \leq P_n = \frac{1}{n}\binom{3n}{n-1}. \tag{89}$$

[Here the expression in parentheses means the number of combinations of 3n things taken (n-1) at a time.]

From (18), recalling that its left member has purely non-negative coefficients, we see that

$$\frac{x[3 + 2x\, s(x^3)]^2}{4} \tag{90}$$

is less than, equal to, or greater than 1, according as x is less than, equal to, or greater than σ.

Since

$$\frac{1}{n}\binom{3n}{n-1} > \frac{1}{n+1}\binom{3n+3}{n}\frac{4}{27} > \frac{1}{n+2}\binom{3n+6}{n+1}\left(\frac{4}{27}\right)^2 > \cdots,$$

$$S_{n+1}x^{n+1} + S_{n+2}x^{n+2} + \cdots < \frac{1}{n+1}\binom{3n+3}{n}\frac{x^{n+1}}{1-\frac{27}{4}x},$$

or

(91) $$\overset{n}{s}(x) < s(x) < \overset{n}{s}(x) + \frac{1}{n+1}\binom{3n+3}{n}\frac{x^{n+1}}{1-\frac{27}{4}x},$$

providing $0 < x < \frac{4}{27}$.

Since (90) contains only $s(x^3)$, (91) is useful if $0 < \sigma^3 < \frac{4}{27}$. (Pólya has determined that $0.30 < \sigma < 0.31$, so these inequalities are certainly fulfilled.)

Let

$$\phi(x) = \overset{n}{s}(x^3)$$

and

$$\psi(x) = \overset{n}{s}(x^3) + \frac{1}{n+1}\binom{3n+3}{n}\frac{x^{3n+3}}{1-\frac{27}{4}x^3}.$$

Hence, if $x_1 < x_2$, and if

$$\frac{x_1\left[2x_1\psi(x_1) + 3\right]^2}{4} < 1,$$

while

$$\frac{x_2\left[2x_2\phi(x_2) + 3\right]^2}{4} > 1,$$

then $x_1 < \sigma < x_2$.

Using this method, the author has determined that

$$0.304215 < \sigma < 0.304220,$$

or, correct to five decimal places,

(92) $$\sigma = 0.30422.$$

In evaluating b, one needs the approximate value of $s'(\sigma^3)$.

If $|x| < \sigma$,

(93) $$s'(x) = \sum_{n=1}^{\infty} nS_n x^{n-1}.$$

Since $\sigma^3 < \sigma$, (93) is valid for $x = \sigma^3$.

Further,

(94) $$n\,S_n x^{n-1} + (n+1)S_{n+1}x^n + \cdots < \frac{n}{2n+1}\binom{3n}{n}\frac{x^{n-1}}{1-\frac{27}{4}x}.$$

Using (93) and (94), the author has determined, to four decimal places,

(95) $$s'(\sigma^{3}) = 1.0616.$$

Likewise, the use of (25), (93), and (95) yielded

(96) $$b = 1.228.$$

Using these values, one can make the following comparisons for $n = 20$.

TABLE 6

	Calculated Value	Asymptotic Approximation
S_{20}	82,300,275	8.4×10^{7}
I_{20}	19,059	1.9×10^{4}
M_{20}	82,281,216	8.4×10^{7}
A_{20}	46,244,031	4.6×10^{7}
B_{20}	225,555	2.7×10^{5}
C_{20}	46,018,476	4.6×10^{7}
T_{20}	3,396,844	3.5×10^{6}
J_{20}	10,306	9.7×10^{3}
N_{20}	3,386,538	3.5×10^{6}

The author is indebted to Professor E. S. Allen for his many valuable suggestions during the preparation and revision of this paper.

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THE GROWTH-REGULANT, HERBICIDAL AND PHYSICAL PROPERTIES OF 2,4-D AND RELATED COMPOUNDS

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The herbicidal action of 2,4-dichlorophenoxyacetic acid (2,4-D) is appreciably different from that of other chemicals. It probably kills plants by regulation of growth, stimulation of meristems and exhaustion of food reserves rather than by direct necrosis and dehydration of exposed tissues. Since it does accelerate vital physiological processes of the cells, any extensive modification of its chemical properties might be expected to interfere with its control over biological activity.

Considerable data were acquired on the relationship of chemical structure to growth regulation and herbicidal potency in some tests begun in May, 1944. The writers became aware of the destructiveness of 2,4-D while confirming some of the pioneering observations (23,7) on the growth regulation of tomatoes. The assistance of organic chemists was solicited after one of us (O.L.H.) became convinced that 2,4-D should be used as a selective herbicide. Apparently several other investigators (5,6,8,16) had reached similar conclusions and had begun research on 2,4-D before Hamner and Tukey (4) announced that it could be used to destroy bindweed under field conditions.

Over 50 compounds were synthesized and tested in seeking potent herbicides, in defining the active nucleus of 2,4-D, and in obtaining formulations that could be readily dispersed in water. The amine salts of 2,4-D were found to have the desired properties; so they were introduced to the commercial trade in 1945 and the rather voluminous data were filed away and practically forgotten. In the past two years, however, many of the botanists and crop specialists who have been called upon to evaluate 2,4-D have expressed a need for more basic information on the chemistry of the 2,4-D compounds being offered to the public. The brief report submitted to the North Central States Weed Control Conference at Springfield (10) elicited many requests for detailed information; so the essential data obtained in a series of greenhouse experiments have been summarized in this paper.

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* The work reported here was done while the authors were members of the staff of the Agricultural Chemical Research Laboratories, Naugatuck Chemical Division of U. S. Rubber Company, Bethany 15, Connecticut. They wish to express their appreciation to the management of U. S. Rubber Company for releasing the data for publication. So many chemists contributed their time and ingenuity to these studies that it is difficult to assign credit. It is fair to state, however, that these studies would not have been completed without the stimulus and cooperation of the following: P. T. Paul, Paul Mader, R. W. Beattie, W. D. Harris, N. K. Sundholm, and F. R. Valentine.

MATERIALS AND METHODS

Fifty-three chemicals were synthesized and tested during 1944 and 1945. These materials, with the exception of 2-chlorophenoxyacetic acid and 4-chlorophenoxyacetic acid (which were purchased from the Eastman Chemical Co.), were synthesized and purified by collaborating chemists. Preliminary tests were made on the compounds individually or in small groups as received. They were then assembled for final evaluation under identical conditions. The following compounds listed under the codes assigned to them in this paper were used:

Code	*Chemical tested*
C 1	Allyl-2-naphthyl ether
C 2	1-chloro-2-naphthoxyacetic acid
C 3	2,4-dichloro-1-naphthoxyacetic acid
C 4	2,4-dichlorophenoxyacetic acid
C 5	2-methyl-4-chlorophenoxyacetic acid
C 6	2-chlorophenoxyacetic acid
C 7	4-chlorophenoxyacetic acid
C 8	2,4,6-trichlorophenoxyacetic acid
C 9	2,4,5-trichlorophenoxyacetic acid
C 10	2,4-dibromophenoxyacetic acid
C 11	4-amino-phenoxyacetic acid hydrochloride
C 12	4-nitrophenoxyacetic acid
C 13	4-acetylaminophenoxyacetic acid
C 14	4-anilinophenoxyacetic acid
C 15	2,4-dichlorophenoxyacetamide
C 16	2,4-dichlorophenoxyacetyl urea
C 17	2,4-dichlorophenoxydiethanol amide
C 18	2,4-dichlorophenoxyacet-2,5-dichloroanilide
C 19	N-cyclohexyl-2,4-dichlorophenoxyacetamide
C 20	Sodium-2,4-dichlorophenoxyacetate
C 21	Potassium salt of 2,4-D
C 22	Calcium salt of 2,4-D
C 23	Ammonium salt of 2,4-D
C 24	Ferric salt of 2,4-D
C 25	Cupric salt of 2,4-D
C 26	Diethanolamine salt of 2,4-D
C 27	Morpholine salt of 2,4-D
C 28	Pyridine salt of 2,4-D
C 29	Triethanolamine salt of 2,4-D
C 30	Monobenzylamine salt of 2,4-D
C 31	Hydroxyethyl-ethylenediamine salt of 2,4-D
C 32	Monoallylamine salt of 2,4-D
C 33	Mono-*n*-butylamine salt of 2,4-D
C 34	Di-*n*-butylamine salt of 2,4-D
C 35	Piperidine salt of 2,4-D
C 36	Cyclohexylamine salt of 2,4-D

C 37	Diallylamine salt of 2,4-D
C 38	Tri-*n*-butylamine salt of 2,4-D
C 39	Dimethylamine salt of 2,4-D
C 40	Monoethylamine salt of 2,4-D
C 41	Triethanolamine salt of 4-chlorophenoxyacetic acid
C 42	Triethanolamine salt of 2,4,5-trichlorophenoxyacetic acid
C 43	Triethanolamine salt of 2-methyl-4-chlorophenoxy-acetic acid
C 44	Isopropyl ester of 2,4-D
C 45	*n*-butyl ester of 2,4-D
C 46	β-chloroethyl ester of 2,4-D
C 47	β-hydroxy-α-chloropropyl ester of 2,4-D
C 48	β,α-dichloropropyl ester of 2,4-D
C 49	2,4-D monoester of polyethylene glycol 200
C 50	2,4-D diester of polyethylene glycol 200
C 51	2,4-D monoester of polyethylene glycol 600
C 52	2,4-D monoester of carbowax 1500
C 53	2,4-D diester of carbowax 1500

Sufficient material was weighed to the nearest 0.1 mg. to prepare about 200 ml. of suspension or solution containing 10,000 ppm. The water soluble materials were dissolved in water. The others were dissolved in 20 ml. of acetone, a few drops of Emulfor EL (reaction product of ethylene oxide and ricinoleic acid) was added and the product emulsified in water. Aliquots of the preparations were then diluted to 1,000 and 100 ppm. so as to provide a dosage series of three concentrations.

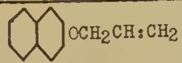
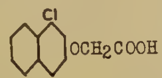
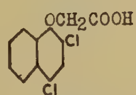
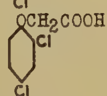
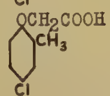
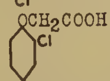
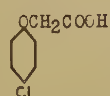
The suspensions were atomized on tomato and bean plants grown in 4-inch pots and placed on a turntable 50 inches from the nozzle of a Devilbiss spray paint gun (9). The spray was applied at 20 lbs. air pressure for 20 seconds so that the material thoroughly covered all leaves and had begun to run on the leaf surface. Duplicate seven-inch tomato plants of the variety Bonny Best and 3 to 5 Pinto bean plants with the first trifoliate leaves partially expanded were used. The chemicals were applied in ascending order of dosages, and the spray gun was thoroughly washed with acetone followed by several rinses in tap water between chemicals. After the plants had been sprayed they were returned to a greenhouse bench and held for observation.

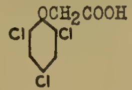
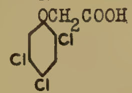
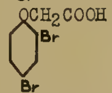
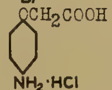
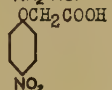
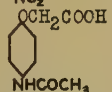
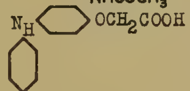
Records were taken periodically, beginning on the first or second day, on the extent of foliage necrosis and epinastic response of petioles by visual estimation. By the fifth day, yellowing of the leaves, swelling of the petioles and stems, and final foliage necrosis could be determined. Final records could be taken on the more active materials after 8 to 10 days; but plants sprayed with weakly active chemicals or at low dosages often were held for 20 to 30 days for final observation on survival of the plants.

Very serious errors were encountered in these trials because of volatility of some of the compounds. The greenhouses were thoroughly ventilated to prevent accumulation of active concentrations of volatile

TABLE 1.

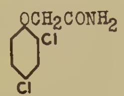
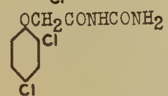
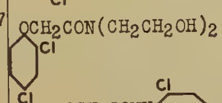
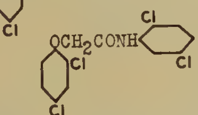
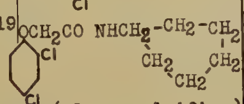
Effect of Modification of the Phenoxy Nucleus on Growth-regulation and Herbicidal Action.

Chemical tested		Dosage used	Response of Pinto beans*				Response of tomatoes*			
			Test 1	Test 2			Test 1	Test 2		
Code	Structural formula	ppm.	36 hrs.	20 hrs.	2 days	8 days	36 hrs.	2 days	5 days	9 days
C 1		10,000	30% DL	DL	DL	DL	Sl. E	DL	M	M
		1,000	Sl. E	Normal	Normal	Normal	Mod. E	Normal	Normal	Normal
		100	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal
C 2		10,000	Normal	M	LM	M	Normal	Normal	Normal	Normal
		1,000	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal
		100	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal
C 3		10,000	30% DL	L, DL	L	DL	Normal	L	L, F	L
		1,000	Normal	Normal	L	F	Normal	Normal	F	Normal
		100	Normal	Normal	Normal	Normal	Normal	Normal	F	Normal
C 4		10,000	Sl.E 20% DL	L, E	E, L	D	E, 5% DL	E	E	D
		1,000	Sev. E	E	E,L,Y	M,DL	Sev. E	E	E,S	D
		100	Sev. E	E	E	Y,S	Sev. E	E	E,S	E,S
C 5		10,000	20% DL,Mod. E				20% DL, Mod.E			
		1,000	Mod. E				Mod. E			
		100	Mod. E				Sev. E			
C 6		10,000	E,YL	L,E	E,M,Y	E,D,L	Sev. E	E	E,F	E,S
		1,000	Sl. E	E	E	Y,S	Sev. E	E	E,F	E,S
		100	Normal	Normal	Normal	Normal	Normal	E	F	Normal
C 7		10,000	E	L,E	L,Y	D	Sev. E	E	DL, E	D
		1,000	E	E	E,Y	E,DL	Sev. E	E	E,S,F	S
		100	E	E	E	Y,S	Sev. E	E	E,S	E,S

Chemical tested		Dosage used	Response of Pinto beans*				Response of tomatoes*			
			Test 1	Test 2			Test 1	Test 2		
Code	Structural formula	ppm.	36 hrs.	20 hrs.	2 days	8 days	36 hrs.	2 days	5 days	9 days
C 8		10,000	20% DL	DL	M	DL	5% DL	M	M	F
		1,000	5% DL	L	L,E	F	Normal	Normal	Normal	Normal
		100	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal
C 9		10,000	E, 50% DL				95% DL,E			
		1,000	Sev. E				Sev. E			
		100	Mod. E				Sev. E			
C 10		10,000	Sl.E,15% DL	E	E,Y,L	DL,Y	Mod. E	E	E	E,S
		1,000	Sev. E	E	E,Y	E,Y	Sev. E	E	E,S	E,S
		100	Mod. E	E	E	E,S	Sl. E	E	E,S	E,S
C11		10,000	Normal	M	Normal	Y	Normal	Normal	Normal	Normal
		1,000	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal
		100	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal
C 12		10,000	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal
		1,000	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal
		100	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal
C 13		10,000	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal
		1,000	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal
		100	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal
C 14		10,000	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal
		1,000	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal
		100	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal

* Responses are coded:
E = epinasty;
F = formative effect on leaves;
Y = yellow leaves;
M = marginal burn;
DL = dead leaves;
L = extensive necrotic spots on leaves;
S = swollen petioles or stem;
D = dead plant.

TABLE 1 (cont.)

Chemical tested		Dosage used ppm.	Response of Pinto beans*				Response of tomatoes*			
			Test 1	Test 2			Test 1	Test 2		
Code	Structural formula		36 hrs.	20 hrs.	2 days	8 days	36 hrs.	2 days	5 days	9 days
C 15		10,000	Mod. E	E	E,Y	D	Sev. E	E	E	D
		1,000	Sl. E	E	E,Y	DL, E	Sev. E	E	E,S	D
		100	Sl. E	E	E,Y	Y,S	Sev. E	E	E,S	E,S
C 16		10,000	Mod. E	E	E,Y,L	D	Sev. E	E	E,S	DL
		1,000	Mod. E	E	E	E,S,Y	Sev. E	E	E,S	E,S
		100	Mod. E	E	E	E,S	Sev. E	E	E,S	E,S
C 17		10,000	Sev. E				Sev. E			
		1,000	Sev. E				Sev. E			
		100	Sev. E				Sev. E			
C 18		10,000	Sev. E	E	E,Y	E,S	Sev. E	E	E,S,F	E,S
		1,000	Mod. E	Normal	Normal	Normal	Sev. E	E	E	E,S
		100	Normal	Normal	Normal	Normal	Normal	E	Normal	Normal
C 19		10,000	Mod. E	E	Normal	Normal	Sev. E	E	E,S	E,S
		1,000	Sl. E	E	Normal	Normal	Mod. E	E	E	Normal
		100	Normal	Normal	Normal	Normal	Normal	E	E,S	E,S
--	None (plus emulsifier)	-	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal
--	None	-	Normal	Normal	Normal	Normal	Normal	Normal	Normal	Normal

compounds. However, one test (No. 1) had to be abandoned after the third day because the greenhouse attendant failed to open the ventilators early in the morning on a warm spring day. The unsprayed controls began to show epinastic responses within two days so all subsequent data were considered unreliable. Similar difficulties were not encountered in the other tests (No. 2) run in midwinter at 60 to 70° F. in a properly ventilated greenhouse.

EXPERIMENTAL RESULTS

After preliminary tests had been completed, all materials were tested on tomato and bean plants under identical conditions at dosages of 10,000, 1,000 and 100 ppm. In the first test (No. 1) made in late spring there was sufficient accumulation of volatile 2,4-D to injure the plants on the third day in the greenhouse; so final data on plant response were discarded. In the other test (No. 2) made in late winter no difficulty was experienced with volatile compounds and very reliable data were obtained over a nine day period.

The data from these two experiments on the effects of modifying the basic nucleus and changing the carboxyl group on growth regulation and herbicidal activity are presented in Tables 1 and 2, respectively.

EFFECT OF MODIFYING THE BASIC STRUCTURE OF 2,4-D

The data in Table 1 show that most of the compounds related to 2,4-D caused pronounced epinasty at all three dosages within 20 to 36 hours. The response was very sharp with petioles bent downward, particularly at the higher dosages of those compounds that did not cause extensive necrosis. There was a reversal of dosage response to epinasty in those chemicals that caused direct necrosis of the leaves. Apparently the killing action at the higher dosages prevented epinasty so that it was expressed only at lower dosages. After a week, many of the plants recovered from leaf burn caused by chemicals without growth regulating properties. The more potent growth regulants caused swollen stems, yellowing of the leaves and death of the plant during this period. The two test plants reacted similarly to the various chemicals. The bean foliage was injured somewhat more easily than tomato, but tomato exhibited a formative effect more readily.

2,4-dichlorophenoxyacetic acid (C 4) was one of the more active compounds included in this test. It caused severe epinasty of both beans and tomatoes within a day at dosages as low as 100 ppm. Lesions developed to the extent of 20 per cent of the leaf area on beans and 5 per cent on tomatoes on plants sprayed with 10,000 ppm. These plants died within a week as did most of the plants sprayed with 1,000 ppm. Plants sprayed with 100 ppm. had swollen stems, yellow leaves and severe epinasty after a week.

The same sequence of events occurred from use of 4-chlorophenoxyacetic acid (C 7) except that there was less foliage necrosis the day after spraying. The final result, however, was practically identical to

TABLE 2.
EFFECT OF MODIFICATION OF THE CARBOXYL GROUP ON THE GROWTH-REGULANT PROPERTIES OF 2,4-D.

Code	Chemical tested Structural formulae*	Dosage used	Response** of Beans	Tomatoes
		ppm.		
C 20	$ROCH_2COONa$	10,000 1,000 100	Sev. E Sev. E Sev. E	Sev. E Mod. E Sev. E
C 21	$ROCH_2COO\ K$	10,000 1,000 100	E Sev. E Sev. E	Sev. E Sev. E Sev. E
C 22	$(ROCH_2COO)_2\ Ca$	10,000 1,000 100	Mod. E Sev. E Sev. E	Sev. E Mod. E Sev. E
C 23	$ROCH_2COONH_4$	10,000 1,000 100	20% DL Sev. E Sev. E	Mod. E Sev. E Sev. E
C 24	$(ROCH_2COO)_3\ Fe$	10,000 1,000 100	Sev. E Sev. E Sev. E	Sev. E Sev. E Sev. E
C 25	$(ROCH_2COO)_2\ Cu$	10,000 1,000 100	Sev. E Sev. E Sev. E	Sev. E Sev. E Sev. E
C 26	$R\text{-}O\text{-}CH_2COONH(C_2H_5OH)_2$	10,000 1,000 100	70% DL Sev. E Mod. E	85% DL, E Sev. E Sev. E
C 27	$R\text{-}O\text{-}CH_2COON\text{-}CH_2CH_2OCH_2CH_2$	10,000 1,000 100	98% DL 25% DL Sev. E	40% DL,Sev. E Sev. E Sev. E
C 28	$R\text{-}O\text{-}CH_2COON$ 	10,000 1,000 100	30% DL Sev. E Mod. E	40% DL, E Sev. E Sev. E
C 29	$ROCH_2COONH(C_2H_5OH)_3$	10,000 1,000 100	95% DL Sev. E Sev. E	Sev. E, 10% DL Sev. E Sev. E
C 30	$ROCH_2COONHCH_2$ 	10,000 1,000 100	30% DL Sev. E Sev. E	Sev. E Sev. E Sev. E
C 31	$ROCH_2COONHC_2H_4NHC_2H_4OH$	10,000 1,000 100	40% DL, F Sev. E Sev. E	Sev. E, 30% DL Sev. E Sev. E
C 32	$ROCH_2COONHCH_2CH{:}CH_2$	10,000 1,000 100	25% DL Sev. E Sev. E	Sev. E, 15% DL Sev. E Sev. E
C 33	$ROCH_2COONH\ C_4H_9$	10,000 1,000 100	45% DL Sev. E Sev. E	Sev. E, 5% DL Sev. E Sev. E

	Chemical tested	Dosage	Response** of	
Code	Structural formulae*	used	Beans	Tomatoes
		ppm.		
C 34	$ROCH_2COON(C_4H_9)_2$	10,000	10% DL, Sl. E	Sev. E
		1,000	Sev. E	Sev. E
		100	Sev. E	Sev. E
C 35	$ROCH_2COONCH_2CH_2CH_2CH_2CH_2$	10,000	85% DL	20% DL. Mod. E
		1,000	Sev. E	Sev. E
		100	Mod. E	Sev. E
C 36	$ROCH_2COONHCH_2CH_2CH_2CH_2CH_2CH_2$	10,000	50% DL	5% DL, Mod. E
		1,000	Mod. E	Mod. E
		100	Mod. E	Sev. E
C 37	$ROCH_2COCN(CH_2CH:CH_2)_2$	10,000	95% DL	20% DL, Mod. E
		1,000	Mod. E	Mod. E
		100	Mod. E	Sev. E
C 38	$ROCH_2COONH(C_4H_9)_3$	10,000	97% DL	Mod. E, 30% DL
		1,000	Mod. E	Sev. E
		100	Mod. E	Sev. E
C 39	$ROCH_2COON(CH_3)_2$	10,000	97% DL	Mod. E
		1,000	Mod. E	Mod. E
		100	Mod. E	Mod. E
C 40	$ROCH_2COONHC_2H_5$	10,000	95% DL, Sl. E	Sl. E
		1,000	Sev. E	Mod. E
		100	Sev. E	Sev. E
C 41	$R^1OCH_2COONH(C_2H_5OH)_3$	10,000	98% DL	Mod. E, 40% DL
		1,000	Mod. E	Mod. E
		100	Mod. E	Sev. E
C 42	$R^2OCH_2COONH(C_2H_5OH)_3$	10,000	10% DL, Sl. E	Mod. E
		1,000	Sev. E	Sev. E
		100	Sev. E	Sev. E
C 44	$ROCH_2COOCH(CH_3)_2$	10,000	100% DL	100% DL
		1,000	Mod. E	Mod. E
		100	Sev. E	Mod. E
C 45	$ROCH_2COOC_4H_9$	10,000	100% DL	95% DL
		1,000	Sev. E	Mod. E
		100	Sev. E	Sev. E
C 46	$ROCH_2COOCH_2CH_2Cl$	10,000	100% DL	90% DL
		1,000	Sl. E	Mod. E
		100	Sev. E	Mod. E
C 47	$ROCH_2COOCH_2CHOHCH_2Cl$	10,000	Mod. E	Mod. E
		1,000	Sev. E	Mod. E
		100	Sev. E	Mod. E
C 48	$ROCH_2COOCH_2CHClCH_2Cl$	10,000	99% DL	70% DL
		1,000	Mod. E	Mod. E
		100	Sev. E	Mod. E
C 49	$ROCH_2COO$-Polyethylene glycol 200	10,000	99% DL	5% DL, Mod. E
		1,000	Sev. E	Mod. E
		100	Sev. E	Sev. E

	Chemical tested	Dosage	Response** of	
Code	Structural formulae*	used	Beans	Tomatoes
		ppm.		
C 50	$(ROCH_2COO)_2$Polyethylene glycol 200	10,000	5% DL	Mod. E
		1,000	Sev. E	Mod. E
		100	Sev. E	Sev. E
C 51	$ROCH_2COO$-Polyethylene glycol 600	10,000	25% DL	Sl. E
		1,000	Sev. E	Sev. E
		100	Sev. E	Sev. E
C 52	$ROCH_2COO$-Carbowax 1500	10,000	5% DL, Mod. E	Mod. E
		1,000	Sev. E	Mod. E
		100	Sev. E	Sev. E
C 53	$(ROCH_2COO)_2$ Carbowax 1500	10,000	80% DL	30% DL, Sl. E
		1,000	Sl. E	Mod. E
		100	Sl. E	Mod. E
--	None	---	Normal	Normal

* The following code was used: R = 2,4-dichlorophenyl
R^1 = 4-chlorophenyl
R^2 = 2,4,5-trichlorophenyl

** Plant responses were coded: E, epinasty; DL, dead leaves. The percentage figures refer to amount of necrotic leaf area as estimated by visual observation.

2,4-D dosage for dosage. 2-chlorophenoxyacetic acid (C 6), on the other hand, was definitely less active. The final response indicates that it is about one-tenth as active as 2,4-D since 10,000 ppm. caused the same symptoms as 1,000 ppm. of 2,4-D; 1,000 ppm. was equivalent to 100 ppm. of 2,4-D; and 100 ppm. was inactive. The replacement of chlorine in the 2-position with a methyl group (C 5) did not seriously reduce activity.

The substitution of a third chlorine on the phenoxy ring affected the activity of the nucleus. 2,4,5-trichlorophenoxyacetic acid (C 9) caused more foliage injury by direct caustic action than did 2,4-D but its growth regulant ability was slightly less. The 2,4,6-trichloro derivative (C 8) was almost inactive. There was some foliage necrosis at 10,000 ppm. but the plants recovered and the only growth regulation was a weak formative effect at 1,000 ppm. on beans and 10,000 ppm. on tomatoes. All plants were normal at lower dosages.

The 2,4-dibromo compound (C 10) was analogous to 2,4-D but weaker in its herbicidal effects. Its growth regulation was comparable to 2,4-D at the various dosages.

Apparently the vital activation derived from chlorine (or other halogens) in the 4-position cannot be obtained from amino (C 11), nitro (C 12), acetylamino (C 13) or anilino (C 14) groups substituted

in this position. All four compounds were totally inactive on both plants in both tests.

The naphthoxy nucleus was not successfully substituted for a phenoxy nucleus. Neither the 1-chloronaphthoxy-2-acetic acid (C 2) or 2,4-dichloronaphthoxyacetic acid (C 3) destroyed plants. There was some foliage necrosis from 10,000 ppm. of C 3 and a mild formative effect. These effects were so mild that this nucleus does not seem to hold any appreciable promise.

Compound C 1 was included in this text as a measure of the effectiveness of an aryloxy nucleus without a carboxyl group on the side chain. This material was chosen from a list of several dozen aryl-alkyl ethers tested elsewhere as insecticides because it was the most phytotoxic. It burned the leaves but the plants recovered and showed no growth response after 8 days. Similar data have been obtained on phenoxy compounds of this class with and without halogens substituted in the ring. It was concluded, therefore, that the phenoxy structure was inactive unless there was a strong negative radical such as the carboxyl group on the side chain.

The carboxyl group can be modified by replacement of the hydroxyl group without destroying activity. The amide of 2,4-D (C 15) was slightly less active in destroying leaves immediately after spraying but its final effects were approximately the same as 2,4-D at comparable dosages. Other amido compounds (C 16, C 17, C 18, C 19) were active. The data show, however, that substitution of an extremely large nucleus such as 2,4-dichloroanilino or cyclohexylamido groups reduced activity. The data on these two compounds, however, may not be a true measure of their biological activity. Large blue needles crystallized while the plants were being sprayed, so much of the chemical may have never reached the plants and that which lodged on the leaf may have been in the form of insoluble needles. Much of the chemical, undoubtedly, never penetrated the leaf.

EFFECTIVENESS OF SALTS AND ESTERS

Thirty-one salts and esters of 2,4-D were evaluated as growth regulants in an experiment conducted under conditions identical to those of test 1 in Table 1. The data obtained on beans and tomatoes sprayed at dosages of 10,000, 1,000 and 100 ppm. agree with Zimmerman and Hitchcock's (23) conclusion that esters and salts of 2,4-D are active growth-regulants. They caused moderate to severe epinasty at all dosages. Some of the compounds were so phytotoxic that epinasty was not expressed fully at the higher dosages where the foliage was severely injured.

The compounds differed in their ability to cause foliage necrosis within 36 hours after applicaton. The amine salts and some of the esters were particularly phytocidal as shown by the data on compounds C 26, C 27, C 29, C 35, C 37, C 38, C 41, C 44, C 45, C 46, C 48, C 49, and C 53. Five to 95 per cent of the leaf area was destroyed. The effective-

ness of the esters of polyethylene glycol (C 49 to C 53) is of interest since the carbowax compounds were used extensively in formulating 2,4-D acids for several years. Zimmerman and Hitchcock (23) introduced these materials and Mitchell and Hamner (12) studied their use as carriers for growth regulants in considerable detail. In the process of heating carbowax to dissolve 2,4-D some esters may have been formed.

TABLE 3

Toxicity of Selected Salts and Esters of 2,4-D and Related Compounds for Beans

Chemical Tested Code	Percentage of Dead Foliage		Condition of Plants Sprayed With 100 ppm 28 days
	10,000 ppm 2 days	1,000 ppm 5 days	
C 4	0	100	3DD, 2 SG*
C 5	50	95	S**
C 7	10	90	1DD, 3 SG
C 9	10	0	1DD, 3 SY
C20	0	95	3DD, 1SG
C21	0	95	3DD, 2SY
C22	0	100	SG
C23	25	100	3DD, 2SY
C25	0	0	S**
C26	100	100	SG
C27	100	100	DD
C28	80	95	SG
C29	100	100	1DD, 4SG
C30	15	95	DD
C31	25	99	2SG, 3DD
C32	50	100	DD
C33	100	95	3DD, 2SG
C34	25	90	S**
C35	100	95	3DD, 1SG
C36	50	95	DD
C37	100	95	3DD, 1SG
C38	95	95	3DD, 1SG
C41	100	95	DD
C42	50	95	DD
C43	100	100	S**
C49	95	100	4DD, 1SG
C50	10	80	1S, 4DD
C51	95	100	DD
C52	100	100	DD
C53	100	100	DD

* DD—Dead and Dried
S—Swollen
G—Green
Y—Yellow
** —Plants in fair condition

The final effect of salts and esters on bean plants was determined in another experiment where selected members were tested. Records were taken over a 28-day period on plants sprayed with 10,000, 1,000 and 100 ppm. Selected data on each dosage at the time differences were most obvious are presented in Table 3.

These data confirm and extend the observations reported in Table 2. The sodium, potassium, calcium and copper salts of 2,4-D and the free acid (C 4, C 20, C 21, C 22 and C 25) killed foliage less rapidly than other materials. Necrosis was most rapid on plants sprayed with amine salts (triethanolamine, C 29; diethanolamine, C 26; morpholine, C 27; pyridine, C 28; mono-*n*-butylamine, C 33; piperidine, C 35; diallylamine, C 37; tri-*n*-butylamine, C 38) and by the esters (monoesters of polyethylene glycol, C 49; monoester and diester of carbowax 1500, C 52 and C 53). At a dosage of 10,000 ppm. all chemicals except C 7 and C 34 killed all leaves within 5 days. When used at a dosage of 1,000 ppm. the compounds killed 80 to 100 per cent of the foliage within 5 days except for the cupric salt of 2,4-D and 2,4,5-trichlorophenoxyacetic acid. Four compounds failed to kill plants at a dosage of 100 ppm. within 28 days. These were 2,methyl-4-chlorophenoxyacetic acid, (C 5); its triethanolamine salt, (C 43); the cupric salt of 2,4-D, (C 25); and the di-*n*-butylamine salt of 2,4-D, (C 34).

The data in Tables 2 and 3 show that the carboxyl group in 2,4-D can be modified by several means without destroying either the growth regulant or herbicidal properties of the 2,4-dichlorophenoxyacetic acid nucleus. The acid may be converted to an amide, ester, metallic salt or amine salt without destroying activity. Apparently the carbonyl group must be retained on the side chain but the hydroxyl group may be substituted with different groupings, within certain limits, without destroying activity.

THE PHYSICAL PROPERTIES OF 2,4-D, ITS SALTS AND ESTERS

The data on salts and esters of 2,4-D in Tables 2 and 3 open many possibilities in creating formulations of 2,4-D that would be serviceable as horticultural spray materials. Salts are more water-soluble than their acids, as a general rule, and esters are oil soluble; so it should be possible to select a member which would be more practical than the free acid. Likewise, it should be possible to regulate volatility since salts are less volatile than acids and most esters are more volatile. With these considerations in mind, tests were made on the solubility and volatility of several of the compounds. Data on the solubility of representative salts are given in Table 4.

The free acid was practically water-insoluble and the salts of calcium, ammonium, sodium and potassium were only slightly better. On the other hand, the salts of diallylamine, diethanolamine, triethanolamine, morpholine and piperidine were exceedingly soluble. Not all amine salts are soluble as shown by the data on salts of allylamine, benzylamine and several other compounds. Of the 10 salts listed in Table 2 as having low solubilities, only two were moderately rapid in killing foliage (column 2, Table 3). The amine salts of low solubility were somewhat more effective than metallic salts of comparable solubilities; but the correlation between solubility and speed of killing foliage is close enough to suggest that penetration of leaves may be

influenced somewhat by solubility. Other factors undoubtedly also affect penetration since the correlations are far from perfect.

These very active amine salts are so soluble that they could be prepared for use in solutions containing 40 to 60 per cent active ingredients. When diluted for spray purposes they remained uniformly dispersed without resorting to extreme agitation as is necessary when wettable powders or quick breaking oil emulsions are used.

Some of the more promising salts and esters of 2,4-D were tested

TABLE 4

THE SOLUBILITY AND MELTING POINTS OF SEVERAL METALLIC AND AMINE SALTS OF 2,4-DICHLOROPHENOXYACETIC ACID AND RELATED COMPOUNDS.*

Salt tested			Physical properties	
Code No.	Phenoxyacetic acid nucleus	Type of salt formed	Melting range	Solubility of salt in water
			°C	gm/100 ml.
C 34	2,4-dichloro	Di-*n*-butylamine	107–109	1.2 @ 31.5°C
C 32	2,4-dichloro	Allylamine	106–107	1.2 @ 31.5°C
C 30	2,4-dichloro	Benzylamine	138–139	1.6 @ 31.5°C
C 33	2,4-dichloro	Mono-*n*-butylamine	93–94.5	1.8 @ 30.5°C
C 38	2,4-dichloro	Tri-*n*-butylamine	30	1.8 @ 30.5°C
C 36	2,4-dichloro	Cyclohexylamine	148–149	2.0 @ 31.5°C
C 20	2,4-dichloro	Sodium		3.5 @ 20.0°C
C 23	2,4-dichloro	Ammonium		3.5 @ 20.0°C
C 21	2,4-dichloro	Potassium		7.0 @ 20.0°C
C 31	2,4-dichloro	Hydroxyethyl-ethylene diamine	135–135.5	9.1 @ 31.5°C
C 35	2,4-dichloro	Piperidine	131–132	230 @ 31.0°C
C 27	2,4-dichloro	Morpholine	136–138	220 @ 30.0°C
C 29	2,4-dichloro	Triethanolamine		440 @ 32.0°C
C 26	2,4-dichloro	Diethanolamine	94–94.5	480 @ 30.0°C
C 37	2,4-dichloro	Diallylamine		710 @ 32.0°C
C 41	4-chloro	Triethanolamine	93–94	460 @ 32.0°C
C 42	2,4,5-trichloro	Triethanolamine	113–116.5	98 @ 32.0°C
C 22	2,4-dichloro	Calcium		0.04 @ 30.0°C
C 4	2,4-dichloro phenoxyacetic acid			0.04 @ 20.0°C

* Data provided by Paul Mader.

alongside the free acid on poison ivy, pastures, lawns, and wheat fields in 1945. The dangers attendant to their use were immediately discovered. Beans and tomato plants were injured 50 yards from treated grass plots. Ornamentals and grapes around lawns frequently suffered severe epinasty and malformation of the leaves. Some of these injured plants could not have been exposed to spray drift; so it was deduced that sufficient chemical was volatilizing from sprayed plots during the heat of day to produce toxic concentrations of gases near the susceptible plants.

The volatility of 2,4-D compounds was tested in an apple orchard.

Blocks of sod 1,600 sq. ft. in size were sprayed with the triethanolamine salt of 2,4-D and the free acid at the rate of 1.5 lbs. of acid per acre. Four hours later six-inch tomato plants in pots were set on inverted saucers in the various plots. All plants placed in the plots sprayed with free acid showed epinastic bending of the petioles within 20 hours and very marked formative effect after a week. There was no epinasty in the triethanolamine block but a very mild formative effect was observed on some of the plants.

More precise data on relative volatility was secured by spraying the inside of 4-liter beakers with suspensions of the acid, ethyl ester or triethanolamine salt at concentrations of 1,000 ppm. 2,4-D until the walls were thoroughly covered. After the beakers were dry they were fitted with a screen innerlining, inverted over 4-inch tomato plants growing in 2.5-inch pots on a greenhouse bench. The temperature of the greenhouse varied from a maximum of 85° F. in late afternoon to 70° F. at night. After 10 minutes of exposure the first group of plants was replaced by another set. These in turn were replaced after one hour and the third group remained in the jars for 16 hours. The wire screen

TABLE 5

EFFECT OF VOLATILE MATERIAL FROM DIFFERENT 2,4-D COMPOUNDS ON TOMATO PLANTS HELD UNDER BEAKERS.

Compound sprayed on inside of beaker	Reaction of plants exposed*		
	10 min.	1 hour	16 hours
2,4-dichlorophenoxyacetic acid	F	E,F	Sev. E,S
triethanolamine salt of 2,4-D	Normal	Normal	Sl. F
ethyl ester of 2,4-D	E,S,DL	E,S,DL	E,S,DL
water (check)	Normal	Normal	Normal

* Reactions coded as: F, formative effect; E, epinasty; S, swelling.

protected the leaves from direct contact with the spray deposit on the beaker; so the growth responses recorded in Table 5 were due to volatile materials released from the spray deposits.

The plants under the beakers sprayed with the triethanolamine salt of 2,4-D were not affected by exposure for 10 minutes or an hour. Apparently sufficient 2,4-D was released after 16 hours to cause a mild formative effect (deformation) of young leaves. In distinct contrast to this, the free acid induced a formative effect after 10 minutes exposure, and pronounced epinasty after one hour. The ester apparently volatilized even more rapidly than the free acid since test plants exposed for only 10 minutes showed epinastic response, lesions on the leaves and, eventually, sufficient stimulation of cambium in the petioles and stems to cause swelling.

DISCUSSION

These data show that there are dozens of compounds related to 2,4-dichlorophenoxyacetic acid that are effective herbicides and growth regulants. These data on spray applications, to a surprising extent, confirm the original observations on lanolin pastes by Zimmerman and Hitchcock (23) and the screening tests by Thompson *et al.* (19) obtained by entirely different techniques. Any conclusions, however, on these growth regulants must be qualified to the extent that only two test plants were used and all tests were run under greenhouse conditions on tender, lightly cuticularized foliage. Further refinements in the experiments such as use of more dosages or use of molar concentrations might have been desirable but would not have altered appreciably the general conclusions. A dosage series based on dilutions by tenths is necessary where such diverse reactions are being studied and the chemicals may be active at such low dosages.

All the evidence obtained in these experiments supports the general conclusion that the major herbicidal effect of 2,4-D is correlated with its growth-regulant properties that stimulate meristems (2,18,20) and change cellular physiology in several respects (3,11,15,17). Those compounds that caused foliage necrosis at high concentrations but were weak growth regulants rarely destroyed plants. Strong growth regulants with moderate caustic action usually destroyed the plants if given sufficient time. Since so little is known about the mechanism of these growth-regulant effects it is impossible to explain why moderate changes in chemical structure affect the properties of the compound. All that can be done in this paper is to describe what happened when compounds were used with different substituents on the phenyl ring, a naphthyl ring replaced the phenyl ring or the carboxyl group was modified.

Apparently halogenation in the 4-position is very essential to strong activity even though Slade *et al.* (16) have obtained good weed control with different methylphenoxyacetic acid compounds. Their data are so different from those reported herein on the several compounds also used by them, however, that they are not considered as on a comparable basis. The 4-chloro derivative was practically equivalent to 2,4-D but the 2-chloro derivative is only about one-tenth as active, a relationship that confirms other reports (23,16,19). If a third chlorine is substituted the molecule is different from 2,4-D in several respects. 2,4,5-trichlorophenoxyacetic acid is more caustic to foliage but may be slightly less active as a growth regulant. 2,4,6-trichlorophenoxyacetic acid is practically inactive, an observation that supports the conclusion of Muir *et al.* (13) that both positions ortho to the acetic acid radical cannot be blocked without destroying activity. Again, the summary of Slade *et al.* (16) claiming that of 2,4,6-trimethylphenoxyacetic acid is very active is in conflict with this general conclusion.

Bromine may be used as an activating agent but 2,4-dibromophenoxyacetic acid is slightly less active than 2,4-D as a herbicide. Groups other than the halogens such as the anilino, amino, nitro,

acetylamino radicals do not activate the phenoxy-nucleus when substituted in the 4-position.

The naphthoxy nucleus does not hold much promise as a herbicide, insofar as the limited data on the two chlorinated derivatives that were tested can be judged. Although the β-naphthoxyacetic acid is a recognized growth regulant (22,1) with strong ability to induce formative effects, it does not operate effectively as a herbicide at low dosages. It is doubtful whether any of the naphthoxyacetic acid compounds will challenge the phenoxy analogs even though some may be more effective (16) than those tested herein.

The oxygen linkage between the aryl and acid groups is not sufficient in itself to cause growth regulation. Since various naphthyl- and phenyl-alkyl ethers were inactive it must be concluded that the phenoxy structure is active only when the side chain has some strong negative group such as the carboxyl radicle.

The carboxyl group, however, can be altered without destroying activity. Apparently the hydroxyl group is unessential to vital reactions since the amides, salts and esters were all fully active. If it is postulated that the OH group is necessary for growth regulation it must be concluded that the amides, esters and salts are hydrolyzed, as they may be, after penetrating the plant. It is more logical to assume the phenoxy compounds are active as long as the carbonyl ($C = O$) group is available on the side chain.

It is possible to tailor-make 2,4-D formulations to almost any physical specification without seriously injuring their physiological activity by altering the carboxyl group. Oil-soluble esters and water-soluble salts can be created. Water solubility falls in the following order: amine salts > metallic salts > acid = esters; so almost any degree of solubility can be obtained. Likewise volatility can be controlled by choice of a compound in the series esters > acid > salts. Intermediate gradations in the volatile range may be secured (14) by varying the length of the carbon chain in the esters. The 2,4-D acid has been described as non-volatile (14) but the data reported herein confirm Zimmerman and Hitchcock's (23) observation. The discrepancies in results are believed to be due to the methods of testing employed wherein a temperature and area of chemical exposed varied appreciably.

After consideration of the above data on physical properties, it was decided that the water-soluble amine salts were the most satisfactory compounds to use as herbicides. Specifically, the triethanolamine salt was chosen because of extreme solubility, strong activity, low volatility and economic synthesis. It is interesting to note that triethanolamine was recommended as a solubilizing agent for 2,4-D when this material was first described (23) as a growth regulant.

Subsequent experience in the field has shown that there are certain geographic differences in the performances of esters and salts that were not revealed in these tests but might have been anticipated by sound deductive reasoning. The amine salts have performed up to expectation

in the East and Midwest but in the extremely, dry, hot areas west of the Missouri river the esters may excel. It is suggested that this may be due to mode of penetration. The salts probably penetrate directly through the epidermis (21) independently of the stomata and are most successful in cooler, humid areas where leaf cuticle is thin and the plant is exposed to dew every night. The esters probably penetrate the stomata in a volatile form so they are favored by warm weather and have an inherent advantage over salts on heavily cuticularized leaves. These hypotheses remain to be confirmed since more data are needed on penetration. However, it was amply demonstrated by the data presented in Table 5 that volatile material could penetrate a plant in sufficient quantities to destroy it after exposure for 10 minutes.

SUMMARY AND CONCLUSIONS

The following conclusions regarding the relationship of chemical structure to biological activity in compounds related to 2,4-dichlorophenoxyacetic acid were deduced from the results obtained on 53 compounds applied as sprays in dosage series to bean and tomato plants under greenhouse conditions:

(1) 2,4-dichlorophenoxyacetic acid is fully as active as any other member of the series but some of its salts and esters affect the plants more readily.

(2) The chlorine in the 2-position of 2,4-D contributes little to its activity since 2-chlorophenoxyacetic acid is only about one-tenth as active as 2,4-D. It may be replaced by a methyl group without serious loss of either growth-regulant or herbicidal properties. The only practical significance to this observation is that active compounds such as methoxone may be synthesized from cheap cresol.

(3) The chlorine in the 4-position is essential to the activation of the phenoxyacetic acid nucleus since 4-chlorophenoxyacetic acid is about as active as 2,4-D. This activity as a herbicide and growth regulant was lost when the chlorine in the 4-position was replaced by amino, nitro, anilino or actylamino groups.

(4) The phenoxy ring probably cannot be replaced by a naphthoxy ring without loss of activity. Neither of the chlorinated alpha or beta naphthoxyacetic acids used were active herbicides and growth regulants. They caused foliage burning only at extremely high dosages.

(5) The carboxyl or some other negative group on the side chain is essential to the growth-regulant and herbicidal activity of 2,4-D since various aryl-alkyl ethers were inactive. The phenoxy structure, either chlorinated or not chlorinated is inactive unless it bears a negative grouping on the side chain.

(6) The carbonyl (C = O) group in the carboxyl radical is essential but the hydroxyl group may be replaced in the formation of an amide, salt or ester without destroying the characteristic biological activity.

(7) Since the carboxyl group could be reacted with ammonia, alkalies, amines, or alcohols without injuring the biological activity of 2,4-D, it was possible to prepare highly active formulations with specified degrees of solubility and volatility.

(8) Salts were found to be more soluble and less volatile than the free acid and decidedly less volatile than esters. The amine salts were found to have particularly desirable physical properties so they were relatively safe to use and easy to formulate as sprays.

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THE EMBRYOLOGY OF "GERMLESS" MAIZE[1]

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Received September 26, 1949

Germlessness of the kernel has occurred as a mutant in dent, sweet and popcorn. The recorded instances (2) probably represent a small fraction of the cases noted by maize breeders. The character has not been useful in linkage studies, and few mutant stocks have been maintained. It has been known that a minute embryo may be evident in the so-called germless segregates, but the embryological basis for the great reduction or apparent absence of the embryo has not been studied in detail.

Germlessness may be the result of failure of fertilization, abortion of the zygote, abortion of the embryo during some phase of its development, or incompatibility between the endosperm and embryo. The numerous cases of germlessness that have been observed or suspected do not necessarily have the same morphogenetic basis. Embryo abortion was found to be the basis for germlessness in a genetic stock that was being studied for other characters (4). This observation led to a study of the embryology of that line, as well as of other available genetically distinct, germless lines.

MATERIALS AND METHODS

The first line of maize used in this study was a genetic stock having the "accessory blade" character (4). During the study of the embryology of this character, some degree of embryo abortion was observed, but the collections were not adequate for a complete study. The second germless stock used occurred as a mutant in one of the long-time inbred genetic stocks. The parent line in which this mutant was found has been continued by self-pollination for at least seven generations. The time of occurrence of the mutation for germless seeds is unknown. No genetic tests have been made of this stock other than to determine that it is inherited as a simple recessive. The tentative designation "Germless S" will be used for this line.

Kernels were collected at the intervals after pollination stated in the text. In the case of the "accessory blade" line, the entire ear was

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removed from the plant and the desired sample of kernels was processed. Segregation for embryo abortion was discovered during microtome sectioning. In the subsequent study of Germless S, provisions were made to determine segregation on the ears. One-half of the ear was removed at the desired interval after pollination and the sample of kernels taken from this piece. The remainder of the ear was bagged again and permitted to ripen. The ears that had kernels segregating for the germless character were readily identified at maturity. The method of processing kernels by the dioxan-normal butyl alcohol-chloroform process has been described by Sass (3).

OBSERVATIONS

A clue to the morphogenetic basis for one form of germlessness in maize was found in the embryology of the genetic stock "accessory blade." This material was being studied with reference to abnormalities of the older embryo [3] and the seedling. Only limited collections of very young kernels were made (4).

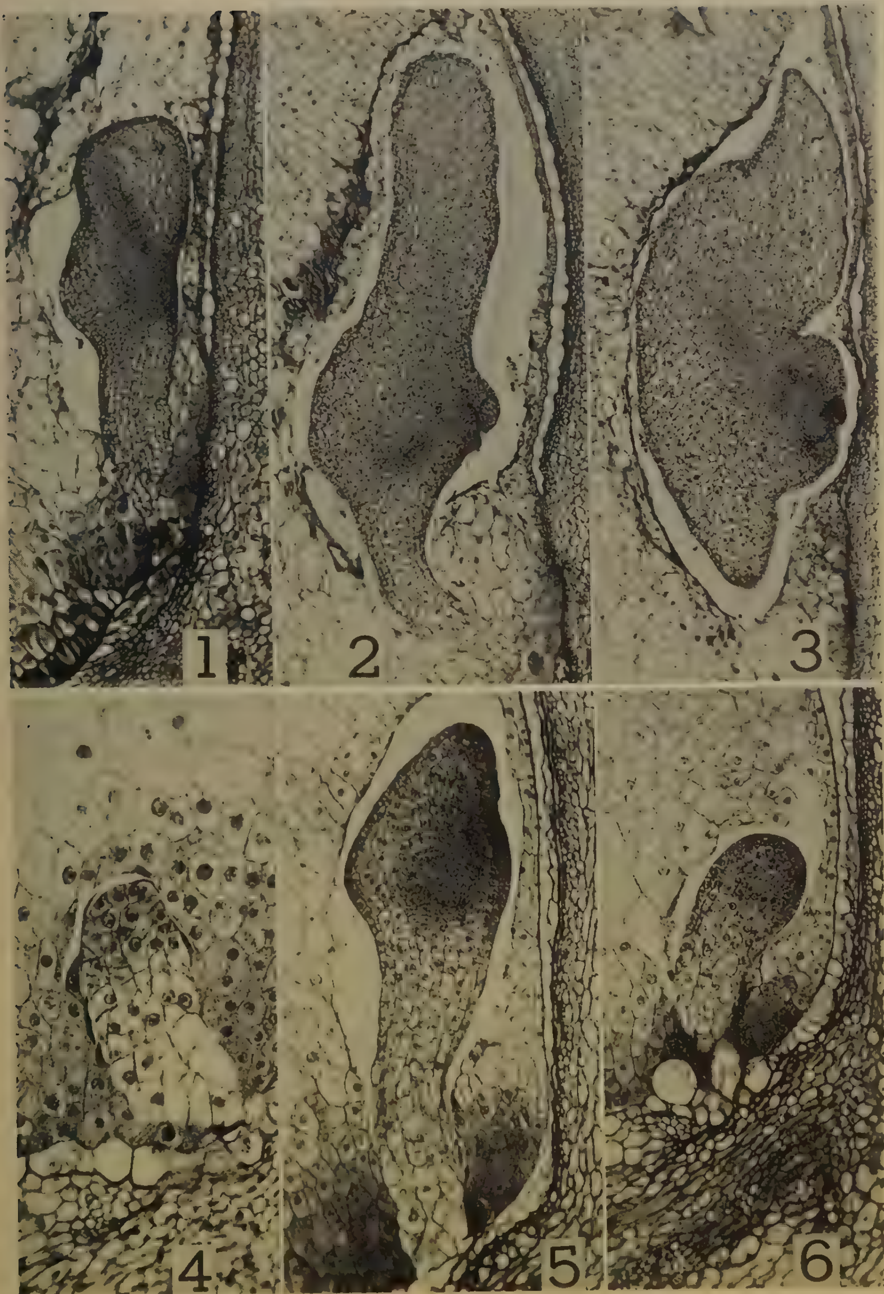
Sections of some kernels collected ten days after pollination show retardation of embryo development. The suspensor is short, and the only indication of organ initiation is the deeper staining of a zone of cells on the domed anterior side of the embryo. This stage is normally attained by the fifth to seventh day and resembles Figure 6. Normal embryos of the same ten-day collection have an elongated suspensor and the coleoptile and stem tip primordia are evident, resembling Figure 5.

Twenty days after pollination, marked retardation of organogeny and some hypertrophy of the embryo may be evident. Only the posterior lobe has been initiated in the embryo shown in Figure 1, and the distal portion is abnormally expanded. Except for this malformation, the stage of development resembles a seven- to ten-day embryo. Another twenty-day embryo (Fig. 2) has a coleoptile primordium, enclosing a domed stem apex. The distal lobe of the scutellum is excessively elongated and thickened. The radicle primordium can be recognized as a deeply stained arc within the embryo.

[3] The term proembryo may be used for the stages prior to the appearance of distinguishable organs. In the present study, a given age class of kernels may have embryos with prominent organs, as well as proembryos in the above sense. In order to simplify terminology, the term embryo will be used in this paper for all post-zygotic stages.

FIGS. 1–3.—Embryos of the Accessory blade line of maize, 20 days after pollination. FIG. 1.—Retarded embryo at 10-day stage of development. Distal lobe is abnormally thickened. 54 X. FIG. 2.—Malformed embryo with coleoptile primordium, and greatly elongated distal lobe of scutellum. 54 X. FIG. 3.—Embryo with highly malformed scutellum. Coleoptile and first foliage leaf primordia are also malformed. 54 X.

FIGS. 4–6.—Embryos of Germless S mutant stock. FIG. 4.—Normal embryo 7 days after pollination. 210 X. FIG. 5.—Normal 10-day embryo, with distinct posterior lobe, and organization of radicle and plumular meristems. 110 X. FIG. 6.—Retarded 10-day embryo, at 5–7 day stage. 110 X.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A more extensive hypertrophy of the embryo, and the distortion of orientation of organs is shown in Figure 3. The scutellum is greatly distorted and its cells are somewhat enlarged. The upper lobe of the coleoptile is abnormally thickened, and its lower lobe is scarcely evident. The first foliage leaf, also abnormally thickened, protrudes below the coleoptile. Varying degrees of hypertrophy and retarded organogeny are evident in this twenty-day collection. A complete study of the embryology was not made because of the complications presented by embryonic characters other than embryo abortion (4).

Further study of embryo abortion was undertaken on a genetic stock of maize, tentatively named "Germless S," which was known to carry the germless character. Retardation of embryo development was found to occur essentially as in the foregoing description. In kernels collected from segregating and nonsegregating ears seven days after pollination, embryo size varies considerably. Most of the variation in size is due to elongation of the suspensor. The distal portion of the embryo is essentially in the same histological stage, regardless of size. A representative embryo is shown in Figure 4. Because of this uniformity of histological condition and variability in over-all size, the potentially abnormal embryos have not been identified in seven-day kernels. Relatively poor survival to maturity occurred with ears that were sampled at seven days and left on the plant to mature, throwing further doubt on the validity of any attempt to estimate at an early stage the degree of embryo retardation in potentially "germless" kernels.

Ears from which samples were taken at least ten days after pollination developed normally to maturity on the plant. Comparisons of embryo development in normal and segregating samples are believed to be valid after the tenth day.

Retarded and normal ten-day embryos are shown in Figures 4 and 5, respectively. The only abnormality at this age seems to be the inhibition or delay of organ formation. Comparative embryo size is not stressed at this point, because the histogenetic stage was found to be a more reliable criterion of development than embryo size.

A representative normal fifteen-day embryo is shown in Figure 7. The coleoptile is nearly closed, and two foliage leaf primordia are present. Retarded embryos show a wide range of variation in the degree of development and the extent of hypertrophy. The greatest retardation observed at fifteen days is shown in Figure 8. This condition resembles a five-day embryo, except for the central zone of deeply stained cells oriented as in a ten-day radicle primordium. A somewhat more advanced

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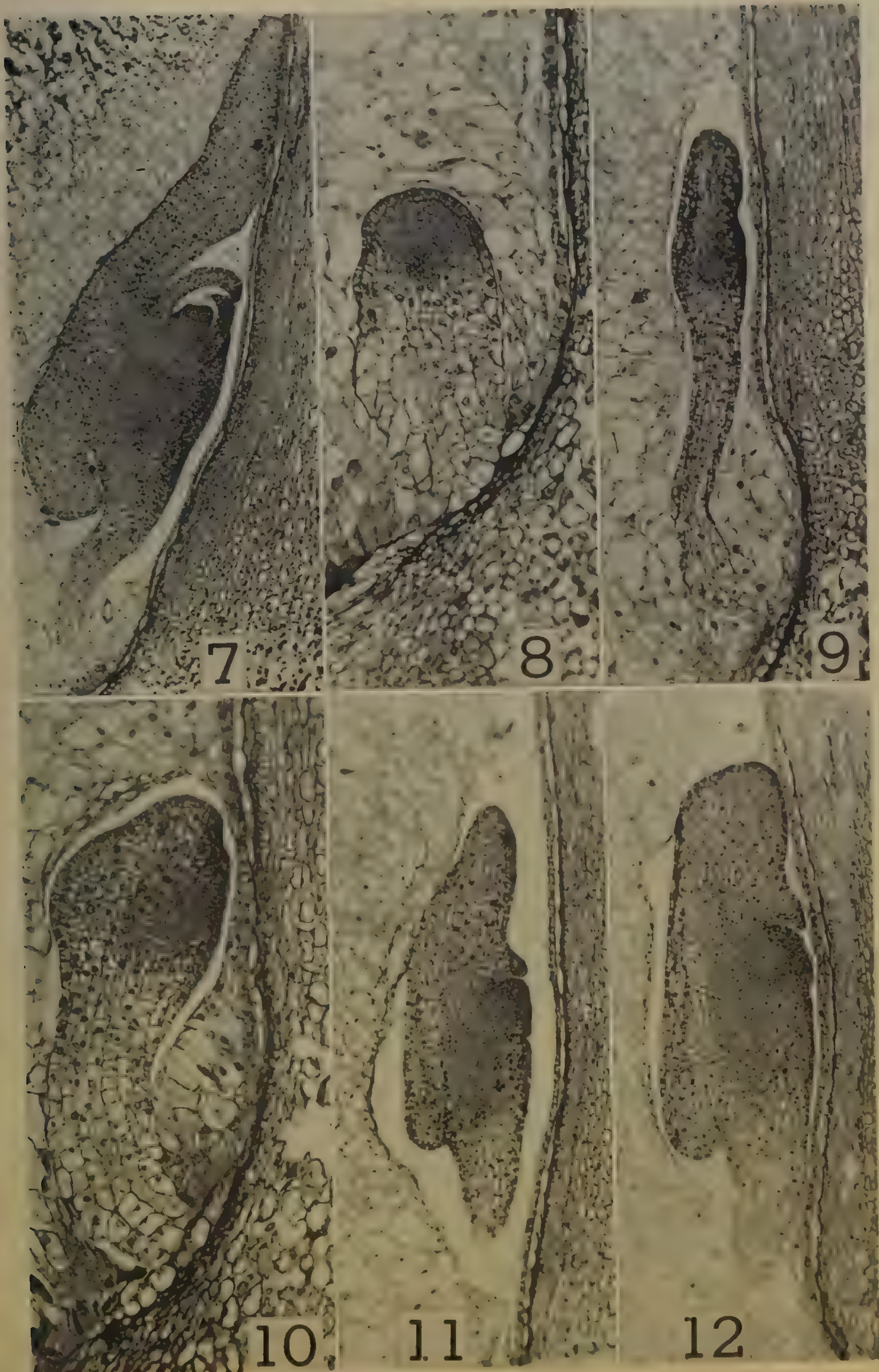
FIGS. 7–11.—Embryos of Germless S mutant stock, 15 days after pollination. FIG. 7.—Normal embryo, with nearly closed coleoptile and two foliage leaf primordia. 43 X. FIG. 8.—Retarded embryo at 5-day stage. 110 X. FIG. 9.—Excessively elongated, retarded embryo at 8–10 day stage. 65 X. FIG. 10.—Apparently normal but retarded embryo at 8–10 day stage. 110 X. FIG. 11.—Embryo with inhibited coleoptile and leaf development. 65 X.

FIG. 12.—Retarded 18-day embryo. Distal lobe of scutellum is malformed, and coleoptile and leaf formation is retarded. 65X.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condition is shown in Figure 10. The suspensor has elongated, the posterior lobe is prominent and there is evidence of plumule axis initiation on the anterior side. This condition resembles the normal seven- to eight-day stage. Figure 9 shows excessive elongation of the suspensor and retarded initiation of the scutellum and plumular primordia. The distal portion resembles the eight- to ten-day stage. In Figure 11, the scutellum and coleoptile are apparently normal in structure but retarded in development. The stem apex is a well defined dome and bears one foliage leaf primordium. The latter, however, is growing downward, showing an obvious disturbance of polarity. This degree of development is normal at ten to twelve days.

An eighteen-day embryo (Fig. 12) shows a retarded scutellum, hypertrophied on the distal lobe, and showing some evidence of necrotic cell compression near the anterior surface. The coleoptile is also greatly retarded in development, and only a trace of the first foliage leaf primordium is evident on the domed stem apex.

Twenty-five days after pollination embryos still exhibit retarded development and hypertrophy, and some necrosis is evident. The small globose embryo in Figure 13 has an endogenous radicle primordium, and an anterior projection where the plumular axis normally arises. The zone of the posterior lobe is distinctly necrotic. In Figure 14, a malformed coleoptile encloses a poorly defined stem apex. Advanced cellular breakdown is evident on the posterior lobe. Extreme malformation of all of the embryo is shown in Figure 16. A central core of cells suggests some stelar differentiation. On the anterior side, a small dome-like projection with a distinctive tunica layer represents the potential plumular axis.

Some approach to normal organogeny at twenty-five days is shown in Figure 15. The closed coleoptile encloses the stem tip, the small primordium of the second leaf, and the abnormally thickened first leaf. The scutellum is hypertrophied and slightly necrotic. In the plane of another section of this kernel, the radicle is well defined.

In ears that are segregating for germless kernels, some kernels seem to lack a microscopically visible germ. Sections of such kernels show a well developed endosperm and a small cavity where the embryo normally occurs. This cavity may contain a quantity of cellular debris, as well as some unidentified granular material (Fig. 17). It is assumed that the most retarded necrotic embryos, like the one shown in Figure 13, undergo disintegration and the embryo space is in part occupied

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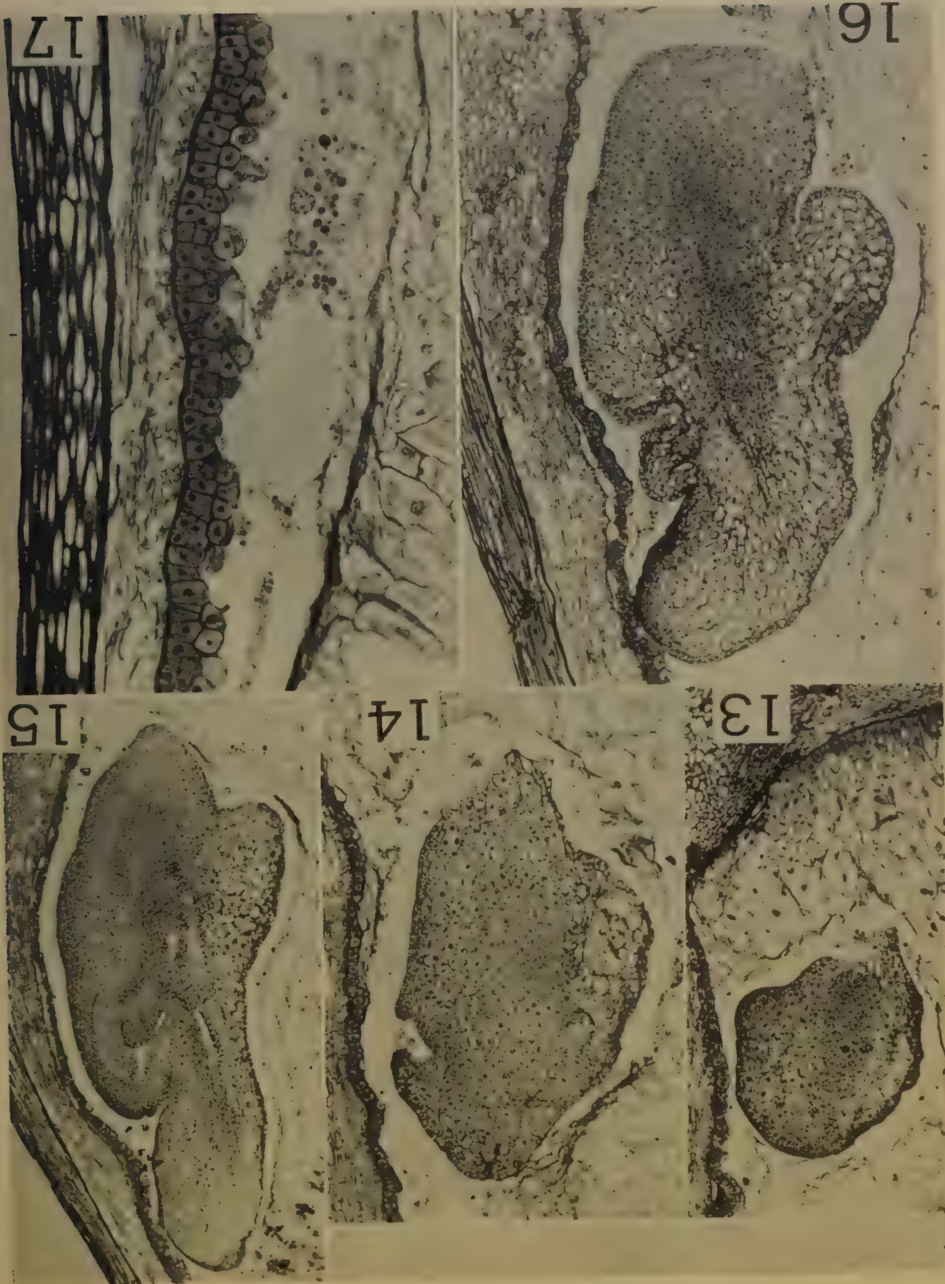
FIGS. 13–16.—Embryos of Germless S line, 20 days after pollination. FIG. 13.—Retarded and malformed embryo with indications of radicle and plumular meristems. Extensive necrosis evident in posterior lobe. 54 X. FIG. 14.—Embryo with plumular apex primordium in partly closed coleoptile. Necrosis evident on posterior lobe. 54 X. FIG. 15.—Embryo with retarded, hypertrophied and necrotic scutellum. One foliage leaf and a minute leaf primordium are present. 32 X. FIG.—Greatly malformed embryo, with rudiment of plumular apex. 54 X.

FIG. 17.—Cavity in a completely germless kernel (25 days), showing debris in cavity, and proliferation of the aleurone. 110 X.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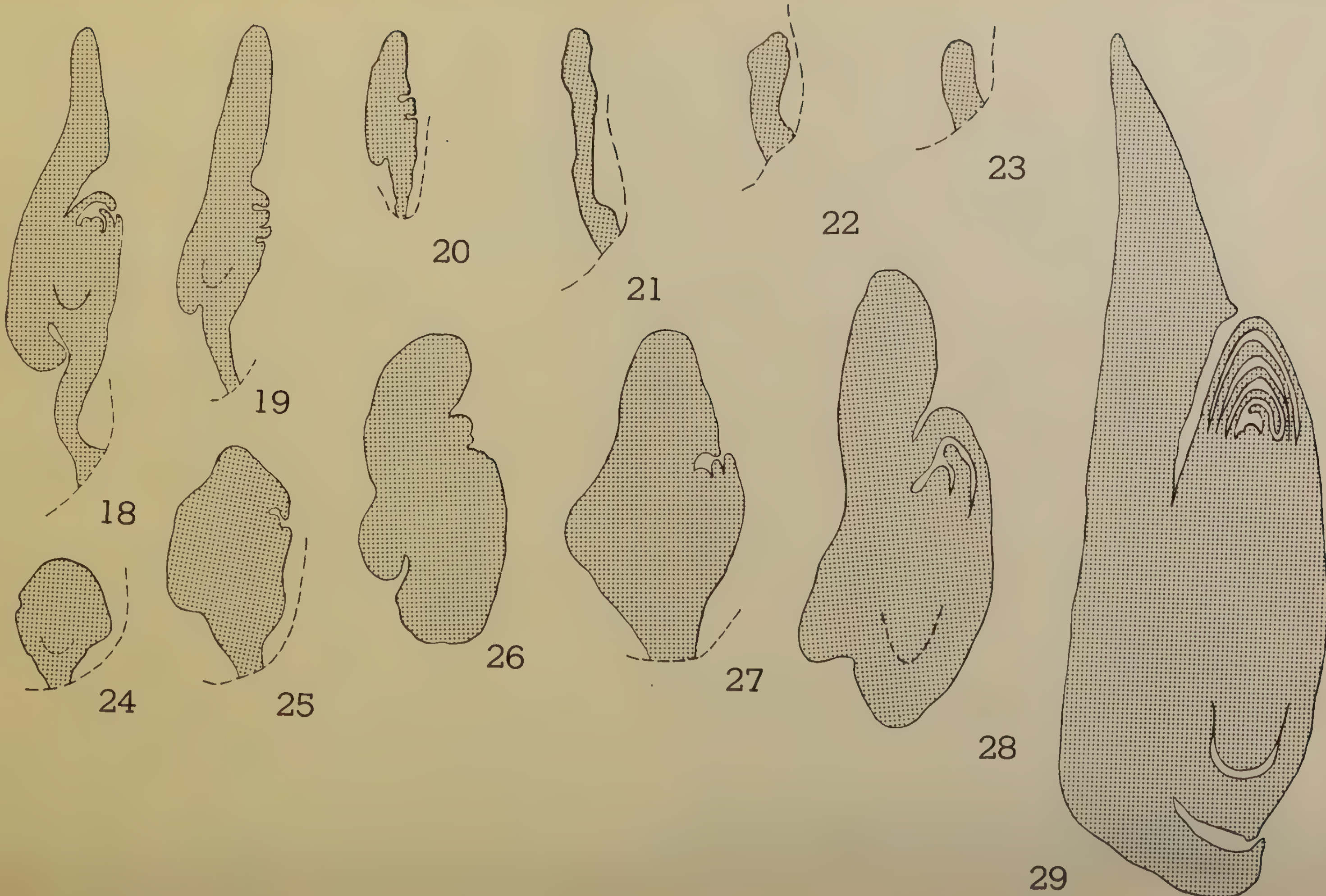
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by the expanding endosperm. Figure 17 also shows the characteristic proliferation of aleurone that is associated with embryo abortion.

The devolpment of the endosperm is normal, regardless of the degree of embryo abortion. The nucellus is invaded by the rapidly growing endosperm, the nucellus disappears by the twelfth day, and starch deposition in the endosperm takes place in a normal manner. In the full-grown kernel the morphology of the endosperm is essentially normal.

DISCUSSION

The failure of seed development in self-fertile plants is most commonly associated with an endosperm aberration. Unfavorable nutritional factors in the defective endosperm bring about an inhibition or breakdown of embryo development. The comprehensive and critical review by Brink and Cooper (1) stresses the importance of this endosperm-embryo balance in seed development.

The two lines of maize used in the present study represent a type of embryo failure that is not associated with morphological abnormality of the endosperm. Destruction of the nucellus and development of the endosperm proceed in a normal manner during the period of retarded development and malformation of the embryo. The basis for defective embryos seems to be in the factors that control the initiation, polarity and development of embryonic organs. There is no clue at present to the nature of these factors, which may be auxins, comparable to the substances that operate in the stem apex. The culturing of embryos in vitro may furnish information concerning possible nutritional deficiencies in the environment of the embryo in the kernel. Such deficiencies would have their basis in a chemical deficiency in the histologically normal endosperm.

SUMMARY

The embryology of two mutant stocks of maize has been studied to determine the basis for the "germless" condition of segregates.

The lines "accessory blade" and "Germless S" have essentially similar embryo abortion as the basis for reduced or apparently absent embryo.

Abnormal embryo development becomes unmistakably evident by the tenth day after pollination, as a retardation or inhibition of organ initiation. A retarded ten-day embryo may be no further advanced histologically than a normal five-day embryo.

FIG. 18.—Normal embryo of Germless S line, 15 days after pollination. 17 X.

FIGS. 19–23.—Embryos of Germless S line, showing degrees of reduction in size and organ development, 15 days after pollination. 17 X.

FIGS. 24–28.—Embryos of Germless S line 25 days after pollination, showing varying malformation, reduction in size and retarded organ formation. 17 X.

FIG. 29.—Normal 25-day embryo of Germless S line. 17 X.

Retardation of enlargement and of organogeny persists during the development of the caryopsis. Hypertrophy and necrosis of embryonic organs occur after the tenth day.

Retarded development and necrosis account for the varying degrees of reduction in embryo size, or for apparent absence of an embryo in the mature kernel.

Endosperm development is normal in the "germless" segregates.

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FLORA OF ALASKA AND ADJACENT PARTS OF CANADA [1]

An Illustrated Descriptive Text of All Vascular Plants Known To Occur Within the Region Concerned

PART VIII. GENTIANACEAE TO CAMPANULACEAE

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Received September 27, 1949

43. GENTIANACEAE (Gentian Family)

Annual or perennial, bitter, mostly glabrous herbs; leaves usually opposite; flowers perfect, regular; calyx persistent, 4- or 5-lobed or parted; corolla funnelform, campanulate, club-shaped, or rotate with 4 or 5 lobes and the stamens partly adnate and alternate with its lobes; ovary bicarpellary, 1-celled, superior, with 2 parital placentae; fruit a many-seeded capsule.

1A. Leaves simple and entire.
  1B. Corolla with 1 or 2 nectiferous pits at the base of each lobe ....1. *Swertia*
  2B. Corolla usually without nectiferous pits.
    1C. Corolla rotate ....2. *Lomatogonium*
    2C. Corolla funnelform to campanulate..............3. *Gentiana*
2A. Leaves trifoliate or crenate. (MENYANTHACEAE)
  1B. Leaves trifoliate.................................4. *Menyanthes*
  2B. Leaves simple, crenate..........................5. *Fauria*

1. SWERTIA L.

Simple-stemmed perennials; leaves alternate or opposite; flowers purple or blue; corolla rotate, usually 5-parted, each division bearing a pair of nectiferous pits; stamens inserted at the base of the corolla; style short or none; stigma 2-lobed; capsule ovate; seed margined. (Emanuel Swert was a German herbalist.)

S. perennis L.

Stems 1–6 dm. tall; lower leaves spatulate or oblanceolate, the blades 3–10 cm. long; stem leaves few, smaller, varying to lanceolate; calyx lobes lanceolate, 5–6 mm. long; corolla lobes 10–12 mm. long, often toothed at the apex; capsule a little longer than the calyx; seed strongly wing-margined.

Shumagin I.—Central Alaska—Colo.—Utah. Fig. 839.

[1] Preceding parts of the paper were published in this Journal as follows: Part 1, Vol. XVIII, pp. 137–75, 1943; Part 2, Vol. XVIII, pp. 381–446, 1944; Part 3, Vol. XIX, pp. 133–205, 1946; Part 4, Vol. XX, pp. 213–57, 1946; Part 5, Vol. XX, pp. 297–347, 1946; Part 6, Vol. XXI, pp. 363–423, 1947; Part 7, Vol. XXIII, pp. 137–87, 1949.

2. LOMATOGONIUM Braun.

Slender, branched, glabrous annuals; calyx united at the base only and with 4 or 5 divisions; corolla 4- or 5-parted, the divisions acute and with a pair of narrow appendages at the bases; stamens inserted on the base of the corolla; anthers versatile; ovary with stigma decurrent along the sutures; capsule 2-valved; seed small, numerous.

L. rotatum (L.) Fries. Marsh Felwort.
Pleurogyne rotata (L.) Griseb.

Stems occasionally simple but usually with erect or ascending branches, 1–4 dm. tall; leaves linear, 1–3 cm. long; sepals linear, 3-nerved, acute, about as long as the corolla; corolla white or blue, divided nearly to the base, the segments 10–12 mm. long.

In wet soil, circumpolar, south to N. H. and Colo. Fig. 840.

3. GENTIANA L.

Glabrous annual, biennial or perennial herbs, often with a basal rosette of leaves; Flowers often variable in size on the same plant; corolla 4- or 5-lobed, often with teeth or plaits in the sinuses; stamens included; style short or none; stigmas 2; capsules with numerous ovules. (Gentius was King of Illyria.)

1A. Corolla with plaits in the sinuses.
  1B. Annuals or biennials.
    1C. Dwarf plants with solitary terminal flowers...... 1. *G. prostrata*
    2C. Swamp plants with axillary flowers............. 2. *G. douglasiana*
  2B. Perennials.
    1C. Flowers whitish................................ 3. *G. algida*
    2C. Flowers normally blue.
      1D. Stem leaves 2–4 pairs, dwarf.................. 4. *G. glauca*
      2D. Stem leaves 4–10 pairs, taller................. 5. *G. platypetala*
2A. Corolla without plaits in the sinuses.
  1B. Corolla with a fringe in the throat.
    1C. Stem very short, peduncles elongated............ 8. *G. tenella*
    2C. Stem longer, peduncles short.
      1D. Calyx lobes rounded, much shorter than the tube.................................. 9. *G. auriculata*
      2D. Calyx lobes acute, much longer than the tube. 10. *G. acuta*
  2B. Corolla without fringed crown in throat.
    1C. Flowers small, usually less than 20 mm. long.
      1D. Leaves ovate, corolla little longer than the calyx..................................... 11. *G. aleutica*
      2D. Leaves narrower, corolla proportionately larger.
        1E. Low alpine-arctic plant..................... 13. *G. arctophila*
        2E. Taller plant of lower elevations.............. 12. *G. propinqua*
    2C. Flowers larger.
      1D. Corolla lobes fringed on the sides............. 6. *G. barbata*
      2D. Corolla lobes not fringed....................... 7. *G. tonsa*

1. *G. prostrata* Haenke. Moss Gentian.
Chondrophylla americana (Engelm.) A. Nels.

Stems low, usually more or less procumbent and branched from the base, 2–10 cm. long; leaves numerous, small, closely ascending, faintly white-margined; calyx 8–10 mm. long with 4 scarious-margined

lobes; corolla blue, 4-lobed, 12–20 mm. long; capsule oblong, 7–14 mm. long, long-stipitate, the stipe often projecting beyond the end of the persistent corolla.

Arctic slope—Alba.—Colo.—B. C. Also in Eurasia. Fig. 841.

2. *G. douglasiana* Bong. Swamp Gentian.

Diffusely branched, 10–25 cm. tall, basal leaves elliptic-oblong to ovate-deltoid, up to 1 cm. in length; stem leaves shorter, ovate-deltoid; corolla white or blue, 8–12 mm. long, the plaits conspicuous, usually 2-forked at the apex; capsule obovate, flattened.

In muskegs near the coast, Kenai Pen.—Ore. Fig. 842.

3. *G. algida* Pall. Whitish Gentian.
G. frigida Haenke.
G. romanzovii Ledeb.

Few-flowered, 5–10 cm. tall; leaves mostly basal, rather thick, linear to oblanceolate, 3–10 cm. long, the upper pair of stem leaves connate; calyx up to 2 cm. long, its uneven lobes with 2 teeth or lobes; corolla yellowish white, often tinged blue and purple spotted above, 3–5 cm. long, the lobes triangular, acute, the plaits broad.

East Asia—Seward Pen.—Colo.—Utah—B. C. Fig. 843.

4. *G. glauca* Pall. Glaucous Gentian.

Stems simple, 2–4 cm. tall; basal leaves ovate or obovate, thick, 8–12 mm. long; stem leaves elliptic-ovate; calyx about 8 mm. long, its lobes lanceolate; corolla greenish blue, 15–18 mm. long, the lobes obtuse; plaits entire or with a small lobe.

Alpine-arctic, east Asia—arctic Alaska—Mont.—B. C. Fig. 844

5. *G. platypetala* Griseb. Broad-petaled Gentian.
G. calycosa, G. gormani, and *G. covillei* of reports.

Stems several from the base, 1–4 dm. tall, rather stout and leafy; leaves thick, sessile or partly clasping, oval, obtuse, 15–40 mm. long; calyx about 15 mm. long, parted at one or two sides, each part with 1–3 slender teeth; corolla bright blue, 3 cm. or more long. Our showiest Gentian.

Mostly alpine, Kodiak I. along the coast to Ketchikan. Fig. 845.

6. *G. barbata* Froel. Smaller Fringed Gentian.
G. procera Holm.
G. macounii Holm.
G. raupii Pors.

Stems erect, angled, 25–50 cm. tall; lowest leaves spatulate or oblong-lanceolate, obtuse, the upper stem leaves linear lanceolate and acute; branches 1- to 3-flowered with 2 or 3 pairs of leaves; calyx 15–30 mm. long, unequally cleft into acute and carinate lobes the lobes about as

long as the tube; corolla deep blue, 2–4 cm. long, the 4 lobes with long fringes on the sides; smaller plants are usually unbranched.

Asia—central Alaska—Mackenzie district—N. Y.—Minn. Fig 846.

7. *G. detonsa* Rottb.

G. serrata Gunn.

Stems erect, 10–25 cm. tall, simple or sparingly branched from near the base; basal leaves spatulate to oblanceolate; upper stem leaves lanceolate to linear; calyx lobes not carinate; corolla up to 4 cm. long, the lobes narrow, erose at the tips.

Bering Strait region — Mackenzie district — Greenland — Iceland — north Europe.

8. *G. tenella* Rottb. Slender Gentian.

Stems 2–10 cm. tall, usually branched; leaves oblong or the lowest spatulate, 4–10 mm. long; peduncles at maturity up to 8 cm. long; calyx deeply parted, its lobes foliaceous and somewhat unequal; corolla blue, up to 1 cm. long; capsule narrow, a little longer than the persistent corolla.

Eurasia—west Alaska—Greenland—Colo.—Calif. Fig. 847.

9. *G. auriculata* Pall. Auricled Gentian.

Stems 6–18 cm. tall; lower leaves oblong-lanceolate, the upper ovate; calyx lobes rounded, much shorter than the tube; corolla violet-blue, up to 25 mm. long, its lobes ovate; peduncles wing-angled.

An east Asian species found on Attu Island. Fig. 848.

10. *G. acuta* Michx. Northern Gentian.

Stem slightly wing-angled, 1–4 dm. tall; basal leaves spatulate or obovate, obtuse; upper leaves lanceolate, acute, 2–5 cm. long; flowers blue, numerous, up to 18 mm. long, pedicelled and with 2 sepals wider than the others; corolla lobes usually 5 but often 4 with a fimbriate crown at the base of the lobes. The var. *plebeja* (Cham.) Wittst. differs from the type in having few (up to 6) internodes and blunt lower stem leaves.

Asia—Aleutians—Dawson—Lab.—N. D.—Ariz.—Calif. Fig. 849.

11. *G. aleutica* C. & S. Aleutian Gentian.

Stems 4–8 cm. tall; calyx lobes ovate-lanceolate, 2–3 times as long as the tube; corolla up to 15 mm. long, white, yellowish or violet, the lobes nearly as long as the tube; capsule slightly surpassing the persistent corolla.

Attu I.—Sitka and Juneau.

12. *G. propinqua* Rich. Four-parted Gentian.

Slender annual, usually branched at the base and above, 1–4 dm.

tall, slightly wing-angled, often purplish; basal leaves spatulate, the upper lanceolate, 1–2 cm. long; flowers pedicelled, long and narrow, widely variable in size; the flowers near the top of the plant may be 18 mm. long with some near the base of same plant as small as 4 mm. long; calyx lobes very unequal; corolla normally blue, its 4 lobes acute and sometimes denticulate; capsule a little longer than the corolla. Our commonest Gentian.

Asia—Wiseman—Lab.—Alba.—B. C. Fig. 851.

13. *G. arctophila* Griseb. Arctic Gentian.

Low annual, usually branching at the base, 3–15 cm. tall; basal leaves obovate; stem leaves ovate-oblong and acute; calyx lobes somewhat scarious-margined; corolla up to 2 cm. long, the round-ovate lobes acuminate-cuspidate. Perhaps only an arctic race of *G. propinqua*.

Arctic coast—Alaska Range—Great Bear Lake—Coronation Gulf.

4. MENYANTHES (Tourn.) L.

Perennial bog plant; leaves trifoliate with long petioles; flowers perfect, racemose or paniculate, borne on long scapes; calyx deeply 5-parted, persistent; corolla short funnelform, bearded within, white, usually tinted with rose; stamens with filiform filaments and sagittate anthers; capsule ovoid. (Greek, month and flower.)

M. trifoliata L. Buckbean.

Rootstock stout, scaly; leaflets glabrous, 4–10 cm. long; scape 1–3 dm. long; corolla about 15 mm. long.

Circumpolar, south to Penn.—Iowa—Colo.—Calif. Fig. 852.

5. FAURIA Franch.

Leaves simple, glabrous, reniform, all basal on long petioles; flowers in a close, bracted panicle at the top of a long scape; pedicels enlarged below the calyx; stamens exerted; anthers strongly sagittate.

F. crista-galli (Menz.) Makino. Deer Cabbage.

Menyanthes cristia-galli Menz.

Nephrophyllidium crista-galli (Menz.) Gilg.

Rootstock thick and scaly; leaves evenly crenate, 6–14 cm. broad; calyx lobes about 3 mm. long; corolla white, about 7 mm. long; capsule linear-ovoid, about 12 mm. long.

Asia and Prince William Sound—Wash. Fig. 853.

44. APOCYNACEAE (Dogbane Family)

Our species a perennial herb with acrid milky juice; leaves entire and opposite; flowers perfect and regular; sepals 5, persistent; corolla of 5 partly united petals; stamens 5, inserted on the corolla tube and alternate with its lobes; anthers 2-celled; ovary of 2 distinct carpels with united stigma; fruit of 2 distinct follicles.

APOCYNUM (Tourn.) L.

Stems branched; leaves mucronate; flowers rather small; corolla campanulate, the tube with 5 small appendages in the throat, alternating with the stamens; stamens attached at the base of the corolla, the anthers sagittate and adhering to the stigma; follicles slender; seed with a long coma. (Greek, against dog.)

A. androsaemifolium L. Spreading Dogbane.

A glabrous perennial with spreading branches, 3–6 dm. tall; leaves pubescent on the veins beneath, otherwise glabrous, pale beneath, 3–7 cm. long; sepals lanceolate, 2–3 mm. long; corolla about 6 mm. long, its lobes finally reflexed.

Central Alaska—Que.—Ga.—Ariz.—B. C. Fig. 854.

45. POLMONIACEAE (Phlox Family)

Flowers perfect, regular; calyx of 5 partly united sepals; corolla from rotate to salver-shaped and 5-lobed; stamens inserted on the corolla, often at different levels, and alternate with its lobes; ovary superior, mostly 3-celled; capsule 3-valved.

1A. Leaves pinnately compound........................1. *Polemonium*
2A. Leaves bipinnatifid................................5. *Gilia*
3A. Leaves simple.
  1B. Perennials, calyx not enlarging..................2. *Phlox*
  2B. Annuals.
    1C. Calyx distended and finally ruptured by the
        ripening capsule...........................4. *Microsteris*
    2C. Calyx enlarging but not rupturing in fruit.......3. *Collomia*

1. POLEMONIUM (Tourn.) L.

Our species all perennial herbs; leaves alternate, simply pinnate; calyx campanulate, cleft to about the middle; corolla mostly campanulate but may be almost rotate; stamens inserted near the base of the corolla; ovules several to many, rarely only 1 or 2 to each cell. There has been much confusion regarding the species. (Derivation of name uncertain.) The species are often called Jacob's Ladder or Greek Velerian.

1A. Leaves glabrous or nearly so........................1. *P. acutiflorum*
2A. Leaves viscid-pubescent.
  1B. Corollas 10–15 mm. long...........................2. P. *pulcherrimum*
  2B. Corollas 15 mm. or more long......................3. *P. boreale*

1. *P. acutiflorum* Willd.
   P. occidentale Greene

Stems glabrate below, glandular-pubescent above, 2–8 dm. tall; leaflets 15–27, acute at the apex, 8–35 mm. long; calyx 7–9 mm. long, its lobes lanceolate; corolla blue or purple, rarely white, 15–25 mm. long. A dwarf form with corolla fully 25 mm. long and with very wide corolla lobes occurs in the Bering Sea region. This may be a cross with *Polemonium boreale macranthemum*.

Eurasia—Arctic coast—Mackenzie district—Alba.—B. C. Fig. 855.

2. *P. pulcherrimum* Hook.
P. fasciculatum Eastw.
P. rotatum Eastw.

Stems 1–many from a woody rootstock, usually more or less spreading, often branched, 10–35 cm. tall; leaflets up to 31, orbicular to narrowly ovate, oblique, usually less than 8 mm. long in the common form; calyx 5–8 mm. long, the lobes lanceolate and usually obtuse at the apex; corolla blue with yellow tube and rounded lobes. Var. *lindleyi* (Wherry) nov. comb. (*P. lindleyi* Wherry; Am. Midl. Nat. 27; 748, 1942) is a robust form with leaflets up to 14 mm. long and corollas 12–18 mm. long.

Bering Strait—Yukon—Wyo.—Calif. Fig. 856.

3. *P. boreale* Adams.
P. lanatum Pall.

Stems 1–2 dm. tall, occasionally taller, stout and often quite erect, glandular-pubescent at least near the inflorescence; leaves up to 12 cm. long and bearing up to 25 leaflets; leaflets oval, ovate, or lanceolate, up to 12 mm. long; calyx 7–10 mm. long, the lobes acute; corolla campanulate, 20–25 mm. long. Ssp. *macranthemum* (C. & S.) Wherry of the Bering Sea region has larger flowers and leaflets up to 18 mm. long. Ssp. *richardsonii* (Grah.) nov. comb. (*P. richardsonii* Grah. Edinb. N. Phil. J. 4:175, 1827) is a dwarf, far northern race with small leaves and white anthers.

Eurasia — Mackenzie district — Greenland and Arctic — southeast Alaska. Fig. 857.

2. PHLOX L.

Our species low, diffuse, spreading perennials; leaves mostly opposite and entire; flowers showy, in our species solitary; calyx narrow, of 5 partly united, scarious-margined sepals; corolla salverform with slender tube and spreading limb; seed usually only one in each cavity. (Greek, flame.)

Leaves subulate, corolla white .... 1. *P. hoodii*
Leaves broader, corolla pink to blue .... 2. *P. sibirica*

1. *P. hoodii* Rich. Moss Phlox.

Very densely caespitose from a woody rootstock; leaves sparingly lanate, apiculate, 4–10 mm. long; flowers sessile at the end of the branches; calyx 5–7 mm. long; limb of corolla about 1 cm. across.

Northeast Alaska—Yukon—Mackenzie district—Neb.—Idaho.

2. *P. sibirica* L. Siberian Phlox.

Depressed and loosely, or sometimes densely caespitose; leaves narrow, linear, apiculate, villous pubescent, especially along the margins;

calyx about 10 mm. long, the narrow sepals sharp-pointed; corolla tube about same length as the calyx, its lobes 6–8 mm. long; style almost equaling the corolla tube.

Northeast Asia—Arctic—central Alaska. Fig. 858.

3. COLLOMIA Nutt.

Leaves alternate, entire; flowers in subcapitate clusters at the end of the stem and in the axils of the upper leaves; Calyx with scarious sinuses; corolla funnelform with the 5 stamens unequally inserted on the tube; ovules 1–few in each cell; seeds developing mucilage and spirocles when wetted. (Greek, gluten, for the mucilage of the wet seed.)

C. linearis Nutt.

Stems puberulent, 7–40 cm. tall; lower leaves linear-lanceolate, the upper lanceolate 2–7 cm. long, 2–8 mm. wide; corolla tube yellowish, the limb tinted pink or purple; calyx lobes lanceolate, acuminate; capsule about 4 mm. long.

Central Alaska—Minn.—Colo.—Ariz.—Calif. Fig. 859.

4. MICROSTERIS Greene

Small, usually branched annuals; leaves narrow and entire, the lower ones opposite; flowers small, axillary; calyx 5-cleft, scarious between the lobes; corolla salverform with a slender tube and 5-lobed limb; capsule 3-celled with few large seed. (Greek, small Steris.)

M. gracilis (Dougl.) Greene

Stems 1–4 dm. tall, glandular and puberulent above; basal leaves spatulate, the leaves becoming linear or linear-lanceolate above; 2–6 cm. long; calyx 7–10 mm. long; corolla 10–14 mm. long, the tube yellowish, the limb purplish or violet. Probably introduced.

Haines, and B. C.—Mont.—Wyo.—Calif.

5. GILIA R. and P.

Calyx campanulate, the tube more or less hyaline in the sinuses and bursted by the mature capsule; corolla trumpet-shaped or salverform; capsule usually many-seeded. (Philip Gil was a Spanish botanist.)

G. capitata Dougl.

Stems erect, glabrous or nearly so, up to 6 dm. tall; leaves bi- or tripinnatifid with linear segments; flowers blue, in terminal capitate clusters; lobes of the corolla about equaling the tube.

Occasionally persisting from cultivation. Native of the Pacific states.

46. HYDROPHYLLACEAE (Water-leaf Family)

Annual or perennial, usually hirsute or pubescent herbs; flowers white or blue, regular or nearly so; calyx deeply cleft or divided;

corolla mostly campanulate or funnelform with 5 lobes; stamens 5, attached to the base of the corolla and alternate with its lobes; filaments often bearded; ovary 1- or 2-celled developing into a few- to many-seeded capsule.

Styles united to the apex..............................1. *Romanzoffia*
Styles free at the apex................................2. *Phacelia*

1. ROMANZOFFIA Cham.

Low perennials; leaves chiefly basal, roundish or reniform; flowering stems scapose; corolla campanulate, white or slightly tinted; stamens unequal; ovary 2-celled or nearly so; ovules many. The plants have very much the aspect of *Saxifraga*. (Romanzoff was a Russian who sent Kotzebue to Alaska.)

Calyx and pedicels glabrous...........................1. *R. sitchensis*
Calyx and pedicels pubescent..........................2. *R. unalaschcensis*

1. *R. sitchensis* Bong. Mist Maid.

Only slightly pubescent, 1–2 dm. tall; leaf blades mostly reniform, sometimes orbicular, the base cordate, glabrate, 10–35 mm. wide; corolla about 8 mm. long and nearly as broad; calyx lobes linear-lanceolate, nearly half as long as the corolla; capsule ovoid. *R. minima* Brand appears to be a very depauperate form of this species. It has been collected at Craig.

Kodiak I. east along the coast to Cailf. and Alba.—Mont. Fig. 860.

2. *R. unalaschcensis* Cham.

8–20 cm. tall; leaves similar to those of *R. sitchensis* but viscid-pubescent beneath and on the petioles, up to 33 mm. wide; calyx 5–7 mm. long, at least two-thirds the length of the corolla; capsule pubescent. A rare form with nearly glabrous leaves is the var. *glabriuscula* Hult.

East Aleutians — Kodiak Island group and Vancouver I. — Calif. Fig. 861.

2. PHACELIA Juss.

Leaves various in form, in our species alternate; flowers in scorpoid racemes or cymes, perfect; calyx 5-lobed, slightly enlarging in fruit; corolla white, blue or purple, 5-lobed, appendaged within; stamens 5, the filaments adnate to the tube of the corolla; ovules 2–many on each of the 2 placentae; seeds reticulate or roughened. (Greek, a cluster, referring to the flowers of some species.)

Plant annual or biennial...............................1. *P. franklinii*
Plant perennial..2. *P. mollis*

1. *P. franklinii* (R. Br.) Gray. Franklin Phacelia.

Stems 2–5 dm. tall, softly hirsute, often much branched; leaves similarly pubescent, 3–7 cm. long, pinnately parted into linear-oblong, entire, toothed or incised acute lobes; inflorescence dense; calyx lobes

linear, acute, up to 8 mm. long in fruit; corolla bluish or nearly white, about 8 mm. long; stamens slightly exerted; ovules numerous.

Yukon—Great Slave Lake—Mich.—Wyo.—Idaho—B. C. Fig. 862.

2. *P. mollis* Macbr. Silky Phacelia.

Silky-pubescent throughout; stems 1–4 dm. tall from a branching caudex; leaves 3–10 cm. long, somewhat doubly pinnatifid; inflorescence dense and spike-like; corolla blue, violet or white, 5–6 mm. long; stamens long-exerted, more than twice the length of the corolla.

Haines—Yukon. Fig. 863.

An undetermined species of Phacelia in fruit was collected at Chicken in the Fortymile district in 1941. The stems arise from a thick rootstock, are up to 18 cm. tall, silky-canescent; basal leaves lanceolate, cut more than half way to the midrib into 3–6 pairs of rounded ovate lobes, silky above, more densely so beneath; inflorescence of 1–5 dense, head-like, very silky glomerules.

47. BORAGINACEAE (Borage Family)

Our species all annual, biennial or perennial herbs; leaves alternate, simple, entire and bristly; flowers perfect, mostly regular, in scorpoid racemes or spikes which often unroll like a fern frond; calyx mostly 5-lobed, -cleft or -parted and usually persistent; corolla from nearly rotate to salver-shaped, 5-lobed with the 5 stamens adnate to its tube: ovary 4-lobed, developing normally into four 1-seeded nutlets.

1A. Nutlets with hooked prickles, at least on the margins.
  1B Nutlets spreading or divergent on the low receptacle.... 1. *Cyanoglossum*
  2B. Nutlets erect on elevated receptacle.
    1C. Fruiting pedicels erect............................ 2. *Lappula*
    2C. Fruiting pedicels recurved or reflexed............ 3. *Hackelia*
2A. Nutlets unarmed, often roughened.
  1B. Receptacle flat or merely convex.
    1C. Nutlets obliquely attached......................... 4. *Mertensia*
    2C. Nutlets attached by the very base.................. 5. *Myosotis*
  2B. Receptacle conic or elongated.
    1C. Calyx in fruit much enlarged, veiny-reticulate and folded.................................. 10. *Asperugo*
    2C. Calyx only moderately enlarged in fruit.
      1D. Corolla yellow or orange........................ 7. *Amsinckia*
      2D. Corolla blue or white.
        1E. Nutlets attached below the middle and with a margined, truncate back.................... 6. *Eretrichium*
        2E. Nutlets attached at about the middle, not as above.
          1F. Nutlets more or less keeled on the outer surface, the scar ovate or orbicular....... 8. *Plagiobotrys*
          2F. Nutlets not keeled, the scar linear or dilated at the base........................ 9. *Cryptanthe*

1. CYANOGLOSSUM (Tourn.) L.

Hirsute or hispid tall herbs; basal leaves with long margined petioles; calyx lobes spreading or reflexed; corolla funnelform or salverform, the tube short, the throat closed by 5 scales; stamens included;

ovary separating into 4 diverging nutlets in fruit; nutlets covered with short barbed prickles. (Greek, dog's tongue.)

C. boreale Fern. Northern Wild Comfrey.

Perennial, leafless above, 4–8 dm. tall; upper stem-leaves clasping the stem; corolla blue, 6–8 mm. across; fruiting pedicels recurved; nutlets ovoid-pyriform, 4–5 mm. long.

Liard River Hot Springs—Que.—N. B.—N. Y.—Minn.—B. C.

2. LAPPULA (Riv.) Moench.

Rough-hairy herbs; leaves narrow and pubescent; flowers small, blue, borne in terminal scorpoid racemes; calyx lobes narrow; throat of the corolla closed by 5 scales; nutlets with barbed prickles along the edge and sometimes smaller ones on the dorsal surface.

Marginal prickles of nutlets in 2 rows, their bases distinct....1. *L. myosotis*
Marginal prickles in 1 row, their bases broad and often confluent..2. *L. redowski*

1. *L. myosotis* Moench. European Stickseed.
L. echinata Gilib.

Stems branched, 15–40 cm. tall; leaves narrow, all except the lowest sessile, 1–3 cm. long; pedicels short and not deflexed in fruit; corolla blue, about 2 mm. wide; prickles of the nutlets stout and hooked.

A roadside weed, native of Eurasia but widely naturalized. Fig. 864.

2. *L. redowski* (Hornem.) Greene. Redowski Stickseed.
L. occidentalis (Wats.) Greene.

Similar to *L. myosotis* but the stem unbranched below but with ascending branches above; nutlets papillose-tuberculate on the back with the marginal bristles flat and their bases more or less united.

Central Alaska—Sask.—Mo.—N. M.—Wash. Fig. 865.

3. HACKELIA Opiz.

Biennial or perennial; inflorescence naked or rarely sparsely bracteate; pedicels recurved or deflexed in fruit; style definitely surpassed by the nutlets; nutlets attached by a large oblique submedial ovate or deltoid areola; ventral keel extending over only the upper half of the nutlet.

H. leptophylla (Rydb.) Johnst.

Stems up to 8 dm. tall, finely pubescent with reflexed hairs, leafy, branched above; basal leaves oblanceolate; stem leaves lanceolate, very thin, 1–2 dm. long; inflorescence much branched and many-flowered; corolla blue, 2–3 mm. across; fruit about 5 mm. in diameter; margins of the nutlets with varying linear-lanceolate prickles up to 3 mm. long.

Along Glenn Highway—Mont. and Wyo.

4. MERTENSIA Roth.

Perennial herbs; flowers blue, rather large, borne in terminal racemes or panicles; calyx deeply 5-cleft, persistent; corolla tubular-funnelform or trumpet-shaped with 5 imbricated lobes; stamens with short, often flattened filaments. (C. F. Mertens was a German botanist.)

1A. Trailing seashore plants.
 1B. Corollas 6–7 mm. long .... 1. *M. maritima*
 2B. Corollas 10–11 mm. long .... 2. *M. asiatica*
2A. Not maritime, stems ascending.
 1B. Calyx lobes glabrous .... 3. *M. eastwoodae*
 2B. Calyx lobes pubescent .... 4. *M. paniculata*

1. *M. maritima* (L.) S. F. Gray — Sea Lungwort.
 Pneumaria maritima (L.) Hill.

Pale green, often glaucous, the stems usually forming a loose mat on beach gravel, 2–6 dm. long; leaves fleshy, the lower petioled, the uppermost sessile, 2–6 cm. long; calyx much enlarged in fruit, the lobes becoming broad and orbicular with a sharply pointed apex; nutlets smooth and shining.

Interrupted circumpolar, south to the Aleutians, Queen Charlotte Islands and Mass. Fig. 866.

2. *M. asiatica* (Takeda) Macbr. — Asiatic Lungwort.

Differs from *M. maritima* in the large corolla, long styles and broad filaments.

An asiatic species found on the western Aleutians.

3. *M. eastwoodae* Macbr. — Eastwood Lungwort.

Stems erect, 2–6 dm. tall; cauline leaves elliptic-lanceolate, 2–10 cm. long, 1–4 cm. broad, acuminate, both surfaces strigose with the hairs pointing toward the apex or the upper surface nearly glabrous; corolla 12–15 mm. long, 3–5 times as long as the calyx; nutlets more or less shiny.

Seward Pen.—Kokrines Mts.—Takotna—Lake Clerk.

4. *M. paniculata* (Ait.) Don. — Tall Lungwort.

Plant hirsute throughout, strigose in the inflorescence, 2–7 dm. tall; leaves on sterile branches cordate to oval, often 1–2 dm. long on petioles 15–30 cm. long; stem leaves lanceolate, 4–10 cm. long; calyx lobes from ½ to as long as the corolla tube, the tube about equaling the limb; corolla 12–16 mm. long; nutlets tuberculed and wrinkled. Var. *alaskana* (Britt.) L. O. Will. has narrow leaves, calyx lobes glabrous on the back but ciliate on the margins.

Common, most of Alaska—Que.—Mich.—Iowa—Mont.—Wash. Fig. 867.

5. MYOSOTIS (Rupp.) L.

Rather low herbs; the perfect regular flowers borne in 1-sided

racemes; corolla usually blue, sometimes pink or white, often with an eye, the tube about the length of the calyx, the throat with appendages; nutlets small, smooth and shining. (Greek, mouse ear.)

Hairs of the calyx spreading............................1. *M. alpestris*
Hairs of the calyx appressed............................2. *M. palustris*

1. *M. alpestris* Schmidt subsp. *asiatica* Vesterg. Forget-me-not.

Stems erect, 1–3 dm. tall; basal leaves spatulate or oblanceolate and petioled, 3–7 cm. long; stem leaves linear-lanceolate; corolla bright blue with yellow eye. This is Alaska's official territorial flower.

Arctic coast—Mackenzie district—Alba.—Colo.—B. C. Fig. 868.

2. *M. palustris* (L.) Forget-me-not.

Stems decumbent and rooting at the nodes; flowers similar to *M. alpestris* but later and more continuously produced.

Sparingly escaped from cultivation in several places. Native of Eurasia.

Myosotis arvensis L. a native of Eurasia with flowers 2–3 mm. across has been reported from Mt. McKinley National Park.

6. ERETRICHIUM Schrader

Depressed, pulvinate-caespitose, arctic-alpine perennials; leaves crowded on the short branches; flowers blue with short funnelform corolla; calyx ascending in fruit; nutlets obliquely attached to a conic receptacle, smooth but with an obliquely truncate apex, the truncate portion surrounded by a margin, in ours consisting of teeth with bristly points. (Greek, wool and small hairs.)

1A. Limb of corolla 9–13 mm. across......................1. *E. splendens*
2A. Limb of corolla 5–7 mm. across.
 1B. Flowers raised on distinct sparingly leafy stems......2. *E. aretioides*
 2B. Flower clusters sessile............................3. *E. chamissonis*

1. *E. splendens* Kearney. Showy Eretrichium.

Caudex much branched and forming a mat of numerous short, sterile, leafy shoots and of fewer elongated flowering stems 4–13 cm. long; lower leaves closely appressed, 15–20 mm. by 2–3 mm., tapering to slender petioles, the upper leaves sessile; racemes few-flowered; corolla bright blue; teeth of the nutlets about two-thirds as long as the body.

Alpine, central and northwest Alaska.

2. *E. aretioides* (C. & S.) DC.

Densely villous with long and soft white hairs, often papillose-dilated at the base; leaves 4–10 mm. long; flowering stems 2–12 mm. tall; corolla sky blue; nutlets 1.5 mm. long, the teeth of the border about equaling the body, more or less connate at the base, and bearing minute bristles on margin and apex.

Siberia—arctic Alaska and Yukon—central Alaska—Pribilof Islands. Fig. 869.

3. *E. chamissonis* DC.

Dense and villous; flower clusters at the end of branches sometimes elongated in fruit to 1–2 cm.; flowers and nutlets much as in *E. aretioides* but the bristles at the apex of the teeth on the nutlets show a tendency to be divergent or reflexed.

East Asia, Pribilof Islands and Bering Sea Coast.

7. AMSINCKIA Lehm.

Coarse, rough-hispid biennials; leaves linear to oblong or ovate; calyx persistent; corolla yellow, salver-shaped, with long tube; nutlets rough, bony, attached below the middle. The species found in our region are weeds probably introduced from the Pacific Northwest. (Amsinck was a burgomaster of Hamburg.)

Stems erect, leaves less than 1 cm. wide....................2. *A. lycopsoides*
Stems decumbent with broader leaves....................1. *A. menziesii*

1. *A. menziesii* (Lehm.) Nels. & Macbr. Menzies Fiddle-neck.

Stems branched, 3–8 dm. tall; leaves oblanceolate to long-ovate to lanceolate, strongly but sparsely setulose-hispid; corolla light yellow, about 8 mm. long; nutlets covered with small tubercules but without tessellated ridges.

Introduced, Nome—B. C.—Idaho—Calif.—Introduced further east. Fig. 870A.

2. *A. lycopsoides* Lehm. Fiddle-neck.

Resembles *A. menziesii;* calyx lobes lanceolate, often 1 cm. long; corolla up to 1 cm. long, orange; nutlets with tessellated ridges, interposed with smaller tubercules.

Introduced, Alaska Range—Wash.—Calif. Fig. 870B.

8. PLAGIOBOTRYS F. & M.

Diffusely branched annuals, soft pubescent or hispid; leaves narrow and entire; sepals persistent and often enlarging in fruit; corolla white with yellow crested throat; nutlets rugose, keeled on both sides near the apex. (Greek, oblique and scar.)

1A. Corolla about 1 cm. in diameter....................4. *P. hirtus*
2A. Corolla much smaller.
  1B. Nutlets glossy....................3. *P. cusickii*
  2B. Nutlets dull.
    1C. Calyx densely strigose....................1. *P. orientalis*
    2C. Calyx stiffly hispid....................2. *P. cognatus*

1. *P. orientalis* (L.) Johnst.

Stems usually branched and of spreading growth, 1–3 dm. long; leaves linear, 2–7 cm. by 1–6 mm., strigose-hispid; sepals 2 mm. long

at anthesis, up to 5 mm. long in fruit; corolla 2.5 mm. long, 2 mm. wide; nutlets 1.5–2.25 mm. long, coarsely rugose or reticulated.

Kamchatka—Aleutians—Kodiak and Katmai.

2. *P. cognatus* (Greene) Johnst.
Allocarya cognata Greene

Branching from the base, appressed strigose-pubescent, especially the inflorescence; leaves linear, the lower 2–4 cm. long; racemes loose; fruiting calyces spreading; nutlets acuminate with the scar just above the base.

Probably introduced, native of western America. Fig. 871.

3. *P. cusickii* (Greene) Johnst.
Allocarya cusickii Greene

Diffusely branching, 1–2 dm. tall, canescent with appressed setose-hispid pubescence; nutlets ovate-oblong, vitrous-shining, 1 mm. long, carinate ventrally only, the back with depressed rugae and few tuberculations; scar almost basal, narrowly linear.

Reported from Fairbanks, probably introduced from further south.

4. *P. hirtus* (Greene) Johnst.
Allocarya hirta Greene.

Stems branched, 15–40 cm. tall; lower leaves narrowly linear, 2–8 mm. long, the upper wider; calyx densely brown-villous, almost 3 mm. long in flower; corolla in appearance much like a white Forget-me-not.

Near Juneau, probably adventative from the Pacific Northwest.

9. CRYPTANTHE Lehm.

Hispid branched annuals; leaves narrow and entire; flowers white with 5 crests closing the throat of the corolla; calyx lobes connivent around the nutlets at maturity; nutlets in our species shining, rounded on the back, attached by fully half its length, the scar a groove forked at the base. (Greek, hidden flower.)

C. torreyana (Gray) Greene.

Branched, 1–2 dm. tall; base of many of the leaves pustulate; leaves 10–25 mm. long; corolla about 1.5 mm. wide; calyx in fruit 5–8 mm. long, sepals with a row of very stiff hairs up the center and abundant ascending hairs on the margins; nutlets 2 mm. long.

Introduced at Skagway, B. C.—Alba.—Colo.—Calif. Fig. 872.

10. ASPERUGO (Tourn.) L.

Low procumbent annual; leaves hispid; calyx foliaceous, strongly reticulate-veiny, enlarged in fruit; corolla shorter than the calyx, the limb spreading; nutlets ovoid, granular-tuberculed, keeled, attached by the middle. (Latin, very rough.)

A. procumbens L. German Madwort. Catchweed.

Leaves oblong or spatulate, up to 8 cm. long; corolla blue, about 2 mm. broad; fruiting calyx 8–12 mm. broad.

A weed, native of Europe.

48. LAMIACEAE (Mint Family)

Our species all aromatic herbs with 4-angled stems; leaves simple, opposite or whorled; flowers in axillary clusters or spikes; corolla with a short or long tube, the limb mostly 2-lipped with 2 lobes on the upper lip and 3 lobes on the lower; stamens 4 or one pair abortive; anthers 2-celled; ovary 4-lobed, 4-celled, each cell developing into a 1-seeded nutlet and included in the persistent calyx. This family is often known as *Labiatae.*

1A. Corolla nearly regular, 4– or 5–toothed.
  1B. Anther-bearing stamens 2.........................1. *Lypcopus*
  2B. Anther-bearing stamens 4.........................2. *Mentha*
2A. Corolla bilabiate.
  1B. Calyx with a protruberence on the upper side......3. *Scutellaria*
  2B. Calyx not gibbous on upper side.
    1C. Stamens 4, the upper pair longer than the lower.
      1D. Calyx 5-toothed..............................4. *Glecoma*
      2D. Calyx 2-lipped...............................5. *Dracocephalum*
    2C. Lower stamens longer than the upper.
      1D. Calyx 2-lipped, closed in fruit.................6. *Prunella*
      2D. Calyx 5-toothed.
        1E. Anther-sacs transversely 2-valved...........9. *Galeopsis*
        2E. Anther-sacs not transversely 2-valved.
          1F. Nutlets 3-sided, truncate above...........7. *Lamium*
          2F. Nutlets nearly terete rounded above.......8. *Stachys*

1. LYCOPUS (Tourn.) L.

Mint-like herbs, slightly aromatic, perennial by slender stolons or suckers; leaves lanceolate or oblanceolate with serrate margins; flowers small, in dense, verticillate, bracted clusters; calyx regular or nearly so, 4- or 5-toothed; corolla funnelform or campanulate, nearly equally 5-lobed; upper pair of stamens rudimentary; nutlets 3-angled, truncate, smooth. (Greek, wolf's foot.)

Calyx teeth obtuse, the edges smooth...................1. *L. uniflorus*
Calyx teeth acuminate, finely ciliate on the edges.......2. *L. lucidus*

1. *L. uniflorus* Michx. Northern Bugleweed.

Stem slender, finely puberulent, tuberous thickened at the base, 1–6 dm. tall; leaves glabrous, 25–70 mm. long, distinctly petioled; calyx teeth 4, ovate-lanceolate, not subulate; corolla much longer than the calyx, its lobes spreading.

Wet soil, southeast Alaska—Newf.—N. C.—Neb.—Ore. Fig. 873.

2. *L. lucidus* Turcz. Western Water Horehound.

Stems nearly glabrous or pubescent, especially at the nodes, rather

stout, leafy, 3–9 dm. tall; leaves nearly sessile, 4–12 cm. long; calyx about 3 mm. long with 5 subulate-lanceolate teeth about as long as the tube, ciliate on the margins; corolla scarcely exceeding the calyx.

Circle Hot Springs, B. C.—Neb.—Kan.—Ariz.—Calif. and in east Asia. Fig. 874.

2. MENTHA (Tourn.) L.

Strongly aromatic perennials; flowers perfect, small, purple, pink or white, borne in dense, axillary clusters, often appearing spicate; calyx campanulate, 10-ribbed, 5-lobed, regular or nearly so; corolla nearly regular, 4-lobed, the upper lobe larger than the others; stamens 4; anther-sacs 2, parallel; nutlets ovoid, smooth. (Minthe was a fabled Greek nymph.)

1A. Whorls of flowers all axillary .... 1. *M. arvensis*
2A. Whorls of flowers mostly in spikes.
  1B. Spikes slim, usually interrupted, leaves sessile or nearly so .... 2. *M. spicata*
  2B. Spikes thicker, leaves petioled .... 3. *M. piperita*

1. *M. arvensis* L. — Wild Mint.
M. canadensis L.

Perennial by suckers, pubescent or glabrate; stems erect, usually branched and pubescent, at least along the angles, up to 8 dm. tall; leaves oval or ovate to lanceolate, with the margins crenate to sharply serrate; corolla white to pink. A very variable and widespread species.

Circumboreal, south to Va.—Neb.—N. M. Fig. 875.

2. *M. spicata* L. — Spearmint.

Stems erect, glabrous, 3–7 dm. tall; leaves lanceolate, sessile or nearly so, sharply serrate, up to 7 cm. long; flowers in bracted whorls in an interrupted spike; bracts subulate-lanceolate, ciliate; calyx teeth subulate, about as long as the tube.

Has become established at a few places in Alaska. Native of Europe but widely naturalized.

3. *M. piperita* L. — Peppermint.

Perennial by subterranean suckers; stems glabrous, usually erect, 3–8 dm. tall; leaves lanceolate, dark green, sharply serrate; bracts lanceolate, acuminate; calyx teeth subulate, shorter than the tube.

Found in a few places, native of Europe but widely naturalized.

3. SCUTELLARIA L.

Annual or perennial herbs (some species shrubby); flowers perfect; calyx 2-lipped, the upper with a crest; corolla violet with a 2-lipped limb, the upper lip arched; stamens 4, the anthers ciliate, those of the upper pair 2-celled, those of the lower 1-celled. (Latin, a dish, from the appendaged calyx.)

S. galericulata L. Marsh Skullcap.
S. epilobifolia Hamilton

Perennial by stolons, puberulent, 2–7 dm. tall; leaves short-petioled, sessile near the top of the stem, oblong-lanceolate, crenate, 2–5 cm. long; flowers solitary in the axils; corolla blue, pubescent, 15–20 mm. long.

Swamps and edge of lakes, central Alaska—Mackenzie district—Newf.—N. C.—Neb.—Ariz.—Calif. Fig. 876.

Marrubium vulgare L. Horehound, was once collected at Juneau but has not become established. It is a woolly, usually much-branched plant; leaves oval to nearly orbicular, rugose-veined; flowers in dense axillary clusters. Native of Eurasia.

4. GLECOMA L.

Our species a low, creeping perennial; flowers in axillary verticels; corolla 2-lipped, the tube exerted and enlarged above; upper lip erect and 2-lobed or emarginate; lower lip spreading and 3-lobed; nutlets ovoid, smooth. (Greek name for Thyme or Pennyroyal.)

G. hederacea L. Ground Ivy.
Nepeta hederacea (L.) B.S.P.

Stems puberulent, up to 5 dm. long, the branches ascending; leaves orbicular or reniform, crenate, 1–4 cm. broad; calyx teeth unequal, lanceolate, acuminate; clusters few-flowered; corolla light blue, 14–20 mm. long, the tube 2 or 3 times as long as the calyx.

Southeast Alaska, native of Eurasia.

Nepeta cataria L. Catnip was once collected at Sitka. It is a densely canescent perennial 5–10 dm. tall; leaves coarsely crenate-dentate; flowers in spiked clusters. It is native to Europe and widely naturalized in temperate climates.

5. DRACOCEPHALUM L.

Herbs with blue or purple flowers in axillary or terminal clusters; calyx tubular, 15-nerved, 5-toothed, the upper tooth the largest; corolla 2-lobed and erect, the lower 3-lobed and spreading; anther-sacs diverging; nutlets ovoid, smooth. (Greek, dragon head.)

D. parviflorum Nutt. Dragon Head.

Annual or biennial somewhat branched herb 2–5 dm. tall; leaves 3–8 cm. long, coarsely serrate; bracts pectinate with awl-pointed teeth; corolla light blue, scarcely longer than the calyx.

Central Alaska—Mackenzie district—Que.—N. Y.—Mo.—Ariz. Fig. 877.

6. PRUNELLA L.

Perennial pubescent herbs with petioled toothed leaves; flowers borne in terminal or axillary bracted spikes; calyx 2-lipped, the tube

10-ribbed; stamens 4 but 2 sterile, the fertile stamens with forked filaments, the 2-celled anthers borne on one prong; nutlets smooth. (Derivation of name doubtful.)

P. vulgaris L. subsp. *lanceolata* (Barton) Hult. Heal-all.

Stems procumbent or ascending, sometimes nearly erect, 8–40 cm. tall; leaves oval, ovate or lanceolate, from almost entire to dentate, 2–10 cm. long; spikes dense; bracts broadly ovate-orbicular, cuspidate, with ciliate margins, more or less purplish on the edges; corolla violet, 8–12 mm. long. Var. *aleutica* Fern. with bracts tomentose or lanate on the back and the calyx dark purple occurs on the Aleutian Islands.

Whole species circumboreal, south to Fla.—N. M.—Calif. Fig. 878.

7. LAMIUM L.

Annual or perennial herbs with petioled, usually broad, toothed or incised leaves; flowers strongly 2-lipped, borne in axillary clusters; calyx campanulate, 5-lobed, the upper tooth slightly the larger; corolla slightly inflated in the throat; upper lip concave, entire; lower lip 3-lobed, the lateral lobes small, the middle lobe notched; stamens all fertile. (Greek, throat, from the ringent corolla.)

L. album L. White Dead Nettle.

Perennial, pubescent, rather stout, 3–6 dm. tall; leaves 3–8 cm. long; calyx teeth subulate, spreading, the upper one a little wider; corolla white, 22–25 mm. long, tube about same length as the calyx, contracted at the base, an oblique ring of hairs within.

Established around Juneau. Native of Europe.

8. STACHYS (Tourn.) L.

Our species perennial herbs; leaves toothed or incised; flowers verticillate in the upper axils and an interrupted spike; calyx campanulate with 5 nearly equal teeth; corolla purplish, its tube not exceeding the calyx, the upper lip concave, the lower lip spreading and 3-lobed; anther-sacs divergent; nutlets ovoid or oblong. (Greek, spike, from the inflorescence.)

Upper and lower leaves sessile, middle ones short-petioled. . 1. *S. palustris*
Upper leaves sessile, petioles increasing toward the base. . . . 2. *S. emersonii*

1. *S. palustris* L. subsp. *pilosa* (Nutt.) Epling. Hedge Nettle.

Stems erect, often branched, 3–10 dm. tall; leaves lanceolate or oblong-lanceolate, 4–10 cm. by 1–3 cm., dentate; calyx pubescent and with subulate teeth; corolla 12–16 mm. long, its upper lip pubescent.

Probably introduced, central Alaska—Newf.—N. Y.—Ill.—N. M. and in Eurasia. Fig. 879.

2. *S. emersonii* Piper. Emerson Hedge Nettle.

About 1 m. tall; leaves about 6 pairs, ovate, cordate or subcordate

at the base, coarsely crenate, sparingly pilose-pubescent on both surfaces, 6–7 cm. by about 4 cm.; petioles 2–4 cm. long; internodes exceeding the leaves; flowers 1 or 2 in the axils of the upper leaves, the upper contracted into a leafy-bracted spike; corolla 12 mm. long, purplish, puberulent on the upper lip, the lower lip white-spotted.

Along the coast, Anette I. to Calif.

9. GALEOPSIS L.

Erect branching annuals; flowers borne in verticillate axillary clusters; calyx 5-ribbed with 5 subequal lobes; corolla 2-lobed, dilated at the throat, the upper lip arched and entire, the lower lip 3-cleft, the middle lobe obcordate; anthers 2-celled; nutlets ovoid, slightly flattened, smooth. (Greek, weasel-like.)

G. bifida Boenn. Hemp Nettle.
G. tetrahit Auct.

Stems retrorsely rough-hispid, 4–9 dm. tall, swollen below the joints; leaves ovate-lanceolate, coarsely serrate, 3–10 cm. long; corolla purplish or variegated with white, 15–20 mm. long, about twice as long as the calyx.

An introduced weed, native of Europe and Asia. Fig. 880.

49. SCROPHULARIACEAE (Figwort Family)

Our species all herbs; flowers perfect, sometimes nearly regular but usually distinctly 2-lipped; stamens usually 4, sometimes also a rudimentary fifth, or only 2 fertile, didymous, inserted on the corolla; ovary 2-celled with axial placentae; fruit a 2-celled, 2-valved, usually many-seeded capsule.

1A. Corolla spurred.................................... 1. *Linaria*
2A. Corolla not spurred.
  1B. Stamens 2.
    1C. Corolla elongated and deeply cleft.
      1D. Ovules many................................ 6. *Syntheris*
      2D. Ovules 2.................................... 8. *Lagotis*
    2C. Corolla rotate................................... 7. *Veronica*
  2B. Anther-bearing stamens 4, a fifth filament present.
    1C. Corolla tubular, 2-lipped....................... 2. *Pentstemon*
    2C. Corolla 2-cleft, declined........................ 3. *Collinsia*
  3B. Stamens 4, all anther-bearing.
    1C. Corolla nearly regular, flowers on scapes........ 5. *Limosella*
    2C. Corolla long-campanulate....................... 9. *Digitalis*
    3C. Corolla 2-lipped.
      1D. Stamens not enclosed in upper lip of corolla... 4. *Mimulus*
      2D. Stamens enclosed in upper lip of corolla.
        1E. Anther-sacs dissimilar, the inner one pendulous by its apex.
          1F. Upper lip of corolla much longer than the lower............................10. *Castilleja*
          2F. Upper lip of corolla scarcely longer than lower.............................11. *Orthocarpus*
        2E. Anther-sacs similar and parallel.
          1F. Upper lip of corolla with recurved margins..................................12. *Euphrasia*
          2F. Upper lip of corolla not recurved.

1G. Calyx scarcely or not inflated in fruit... 13. *Pedicularis*
2G. Calyx much inflated and veiny in fruit.. 14. *Rhinanthis*

1. LINARIA (Tourn.) L.

Stems erect, flowers in terminal racemes or spikes; sepals partly united; corolla decidedly 2-lipped, the tube spurred at the base, the throat partly closed by a convex fold; stamens enclosed; capsules short, opening by 3-toothed pores at the apex. (Latin, linum, flax, which some species resemble.)

L. vulgaris Hill. Butter and Eggs.

Perennial by short rootstocks, 2–10 dm. tall, glabrous or pubescent above; leaves linear, entire, sessile, 2–7 cm. long; corolla yellow with orange throat, 2–3 cm. long.

Naturalized in a few places in Alaska and widely elsewhere. Native of Europe.

2. PENTSTEMON Mitchell.

Perennials, mostly branched from the base; leaves opposite; flowers irregular, in terminal racemes or panicles; calyx 5-parted; corolla with elongated tube, the limb 2-lipped; upper lip 2-lobed, the lower 3-lobed; stamens 4, the fifth sterile filament usually bearded; capsule ovoid, 2-valved; seeds numerous. (Greek, five stamens.)

1A. Leaves wide, ovate-lanceolate, serrate..............1. *P. diffusus*
2A. Leaves narrower and entire.
  1B. Flowers 18–25 mm. long..........................2. *P. gormanii*
  2B. Flowers 8–12 mm. long..........................3. *P. procerus*

1. *P. diffusus* Dougl. Diffus Beard-tongue.

Stem glabrous or puberulent, 2–6 dm. tall; leaves glabrate, serrate; inflorescence interrupted; calyx ciliate, 6–8 mm. long, the sepals lanceolate, acuminate; corolla blue or purple, about 2 cm. long.

Hyder—B. C.—Ore. Fig. 881.

2. *P. gormanii* Greene Gorman Beard-tongue.

Stems clustered, decumbent at the base, glandular-pubescent above, 1–5 dm. tall; lower leaves petioled, narrowly spatulate or linear; upper leaves sessile, linear to narrowly lanceolate, 3–8 cm. long; calyx densely pubescent, nearly 1 cm. long, the lobes attenuate; corolla rose-purple; capsule about 1 cm. long.

Central Alaska—Yukon—B. C. Fig. 882.

3. *P. procerus* Dougl.

Stems decumbent at the base, glabrous or slightly pubescent, 10–35 cm. tall; basal leaves oblanceolate or linear-oblanceolate, petioled, glabrous, 4–6 cm. long; inflorescence compact but interrupted below; calyx glabrous, about 5 mm. long, the teeth cuspidate; corolla purplish blue.

Nome and southeast Alaska—Yukon—Sask.—Colo.—Calif. Fig. 883.

3. COLLINSIA Nutt.

Winter annual or biennial herbs; leaves opposite or verticillate; flowers axillary; calyx campanulate, 5-cleft; corolla tube short, the limb 2-lipped; upper lip 2-cleft, the lower lip larger and 3-lobed, the middle lobe keeled and enclosing the stamens. (Zaccheus Collins was a botanist of Philadelphia.)

C. parviflora Dougl. Blue Chickweed.

Stems weak, the branches spreading, 5–30 cm. tall; leaves oblong or lanceolate, 1–4 cm. long, sometimes with a few teeth, the upper often whorled; corolla 5–7 mm. long, blue or whitish; seeds concave.
Haines and Hyder—Ont.—Mich.—Colo.—Ariz. Fig. 884.

4. MIMULUS L.

Annual or perennial herbs with opposite, mostly toothed leaves; flowers axillary and peduncled; calyx angled, unequally 5-lobed; corolla with a reflexed, 2-lobed upper lip and a spreading 3-lobed lower lip; capsule many-seeded, enclosed by the calyx. (Latin, a buffoon, from the grinning corolla.)

Flowers yellow..1. *M. guttatus*
Flowers rose-red......................................2. *M. lewisii*

1. *M. guttatus* DC. Yellow Monkey-flower.
M. langsdorfii Donn.

Stems glabrous below, pubescent above, 1–9 dm. tall; leaves variable, the lower petioled, the upper sessile or clasping, glabrous; calyx 10–15 mm. long, puberulent; corolla 2–4 cm. long, spotted on the lower lip. A variable species. At Craig the author collected dwarf plants less than 1 dm. tall with flowers nearly 4 cm. long growing alongside plants 4–5 dm. tall with flowers 3 cm. long.
Wet places, Aleutians—Talkeetna—B. C.—Mont.—Mexico—Calif. Fig. 885.

2. *M. lewisii* Pursh. Lewis Monkey-flower.

Stems 3–8 dm. tall, more or less viscid-pilose; leaves oblong to lanceolate, dentate, pubescent; flowers on long peduncles; calyx glandular-pubescent, up to 2 cm. long, the teeth triangular and acuminate; corolla 35–50 mm. long.
Hyder—Minn.—Colo.—Ariz.—Calif. Fig. 886.

5. LIMOSELIA L.

Low, glabrous, floating or creeping annuals, or perennial by stolons; leaves basal, entire, slender-petioled; flowers small, white, pink or purplish, borne singly on scape-like peduncles; corolla nearly regular. (Greek, seated in mud.)

L. aquatica L. Mudweed.

Leaves narrowly spatulate or with no blade distinct from the petiole, 2–7 cm. long, the blade ¼ to ⅓ as long as the petiole; peduncles shorter than the leaves; corolla about 2 mm. broad; capsule about 3 mm. long.

Imuruk Basin and Atka I., of wide geographic distribution. Fig. 887.

6. SYNTHERIS Benth.

Low perennials with mostly basal leaves; flowers blue or pink in terminal spikes or racemes; calyx of 4 slightly united sepals; corolla irregularly 2-lipped or wanting; filaments exerted, the anther-cells parallel; capsule short, emarginate; seeds several, flat. (Greek, together and a door, in allusion to the valves of the pod.)

S. borealis Pennell. Kitten tails.

Stems woolly with brown hairs, 5–15 cm. tall; basal leaves cordate in outline, doubly serrate, woolly, especially along the margins; stem leaves few, reduced; flowers in a head-like spike; calyx lobes acute, woolly; capsule emarginate with woolly margins.

Alaska Range and south Yukon. Fig. 888.

7. VERONICA (Tourn.) L.

Annual or perennial herbs; leaves usually opposite but sometimes alternate or verticillate; flowers blue or whitish, axillary, racemose or spicate; calyx mostly 4-parted; corolla rotate, 4-lobed; stamens 2, divergent, inserted at the base of the upper corolla lobe; styles united with a capitate stigma; capsule flat, usually notched or 2-lobed at the apex; seed flat or concave on one side. (Named for St. Veronica.)

1A. Flowers in axillary racemes (*Euveronica*).
  1B. Capsules pubescent.
    1C. Stem less than 5 cm. tall........................ 1. *V. grandiflora*
    2C. Stems 1–3 dm. long............................. 2. *V. chamaedrys*
  2B. Capsule glabrous or nearly so.
    1C. Capsule much wider than long.................. 3. *V. scutellata*
    2C. Capsule nearly as long as wide.................. 4. *V. americana*
2A. Flowers in terminal spikes or racemes (*Veronicella*)
  1B. Perennials.
    1C. Capsule wider than long.
      1D. Corolla pale violet with darker lines........... 5. *V. tenella*
      2D. Corolla whitish with violet lines................ 6. *V. serpyllifolia*
    2C. Capsule as long as or longer than wide, not or only slightly notched.
      1D. Fruiting pedicels 8–11 mm. long............... 7. *V. stelleri*
      2D. Fruiting pedicels 2–5 mm. long............... 8. *V. wormskjoldii*
  2B. Annuals.
    1C. Pedicels longer than the ovate sepals............. 9. *V. persica*
    2C. Pedicels shorter than the lanceolate to linear sepals.
      1D. Leaves narrow, nearly entire.................10 *V. peregrina*
      2D. Leaves wider, crenate-serrate..................11. *V. arvensis*

1. *V. grandiflora* Gaertn. Large-flowered Speedwell.

Pubescent with flat, many-celled hairs; stems decumbent at the

base and with short internodes; leaves 3–5 pairs, broadly oval, obscurely serrate, 15–35 mm. long, contracted into a short petiole; peduncles 1–3, surpassing the leaves, 3- to 8-flowered; corolla blue, 10–15 mm. across.

Kamchatka—Unalaska. Fig. 889.

2. *V. chamaedrys* L. Germander Speedwell.

Stems ascending, slender, pubescent in 2 lines, 1–3 dm. tall; leaves ovate, sessile or nearly so, pubescent, incised-dentate, 12–30 mm. long; corolla light blue, 5–8 mm. across.

Sparingly adventative, native of Europe.

3. *V. scutellata* L. Skullcap Speedwell.

Glabrous or sparingly pubescent; stems slender, weak, 1–5 dm. tall; leaves linear or linear-lanceolate, nearly entire, sessile and slightly clasping, 25–75 mm. by 2–6 mm.; corolla blue, 4–6 mm. across; capsule emarginate at base and apex.

Yukon—Newf.—Va.—Colo.—Calif.

4. *V. americana* (Rof.) Schwein. Brooklime.

Stems glabrous, 2–6 dm. long, usually decumbent and rooting at the base; leaves short-petioled, oblong-lanceolate, 2–8 cm. long, serrate or sometimes almost entire; flowers in long, slender, bracted racemes; corolla blue or nearly white, rarely pink, 4–6 mm. wide; capsule thick, orbicular, slightly notched at the apex.

Growing in water or mud, Aleutians—central Alaska—Newf.—S. C.—Mex.—Calif. and west shore of Bering Sea. Fig. 890.

5. *V. tenella* All. Low Speedwell.
V. humifusa Dickson

Lower portion of stem decumbent and rooting at the nodes, ascending portion 5–30 cm. tall; leaves short-petioled or sessile, suborbicular to ovate, entire or denticulate, 5–18 mm. long, the upper reduced; inflorescence pubescent and often glandular; corolla 3–4 mm. wide; capsule retuse at the apex.

Pacific coast regions of Alaska, circumboreal, south to Maine—N. Y.—Wis.—Colo.—Mex. Fig. 891.

6. *V. serpyllifolia* L. Thyme-leaved Speedwell.

Similar to *V. tenella* but the flowers are smaller, the upper part of the stem is less pubescent and with shorter hairs, and the lower decumbent part of the stem does not root.

Hyder and Haines—Lab.—Ga.—N. M.—Calif.

7. *V. stelleri* Pall. Steller Speedwell.
V. alpina unalaschkensis C. & S.

Stems ascending from a usually decumbent base, 8–35 cm. tall,

hirsute, leafy to the base of the inflorescence; leaves ovate, sharply serrate, up to 4 cm. long but usually much smaller; corolla blue, 8–11 mm. wide; capsules ovate, 7–8 mm. long. Some forms described as *V. stelleri* var. *glabrescens* Hult. and *V. wormskjoldii nutans* (Bong.) Pennell may be hybrids of the two species.

East Asia—Aleutians and Pribilof I.—southeast Alaska. Fig. 892.

8. *V. wormskjoldii* R. & S. Alpine Speedwell.
V. alpina var. *wormskjoldii* (R. & S.)

Stems 1–3 dm. tall, usually simple, pubescent, glandular above; leaves oval or ovate, entire or crenulate, sessile, 1–3 cm. long; corolla blue, campanulate, about 5 mm. wide; capsule emarginate, 4–5 mm. long; a form with wider, distinctly toothed leaves is the var. *nutans* (Bong.) Pennell.

Central Aleutians—Nome—Lab.—N. H.—Ariz. Fig. 893.

9. *V. persica* Poir. Persian Speedwell.
V. buxbaumii Tenore

Stems pubescent, diffusely branched, spreading or ascending, 1–3 dm. tall; leaves ovate or oval, deeply crenate-dentate, 10–25 mm. long; flowers blue, about 1 cm. broad, borne on slender pedicels from the axils of the alternate leaves; calyx lobes spreading; capsule nearly 2 times as wide as long.

Sparingly adventative; native of Europe.

10. *V. peregrina* L. var. *xalapensis* (H.B.K.) Pennell. Neckweed.

Annual, 1–3 dm. tall, more or less pubescent; leaves thick, the lower petioled and opposite, the upper flower-bearing ones alternate; racemes spike-like; corolla whitish, 2–3 mm. wide; capsule orbicular, cordate at the apex, of nearly same length as the calyx lobes.

Probably introduced, widespread in the Americas. Fig. 894.

11. *V. arvensis* L. Corn Speedwell.

Stems pubescent, 5–25 cm. tall; lower leaves petioled and opposite, ovate, crenate; upper leaves sessile, the floral ones reduced to bracts and alternate; corolla blue or whitish, 2 mm. wide, shorter than the calyx; capsule shorter than the calyx, 2 mm. long, obcordate.

Sparingly adventative, native of Europe.

8. LAGOTIS Gaertn.

Perennial glabrous herbs; rootstocks from nearly upright to horizontal; stems scapiform with reduced leaves on the upper part; flowers bluish, in a dense terminal spike, each solitary and sessile in the axis of a bract; corolla 2-lipped, the upper usually crenulate, the lower divided into 2 widely diverging lobes; ovary 2-celled, 2-ovuled.

L. glauca Gaertn.

Stems up to 35 cm. tall, lower leaves ovate to reniform, crenate, up to 15 cm. long; spikes 13–20 mm. thick; stamens shorter than the upper lip of the corolla. Var. *stelleri* (C. & S.) Trautv. has ovate or lanceolate leaves, often with sharp-pointed teeth, the blades seldom more than 6 cm. long and spikes 10–15 mm. thick.

An asiatic species, the head form extending to the Talkeetna Mts. and Bering Sea regions, the variety to the Arctic Coast and Yukon. Fig. 895.

9. DIGITALIS (Tourn.) L.

Tall biennial or perennial herbs; leaves large, alternate; flowers in terminal spikes or racemes, showy; calyx 5-parted; corolla declined, somewhat 2-lipped; stamens ascending, mostly included; seeds numerous, rugose. (Latin, finger of a glove, from the shape of the corolla.)

D. purpurea L. Foxglove.

Stems erect, 6–20 dm. tall, pubescent; basal and lower leaves ovate or ovate-lanceolate, slender-petioled, dentate; upper leaves smaller, becoming sessile; corolla purple to white, spotted within, up to 45 mm. long.

Sparingly escaped from cultivation, native of Europe.

10. CASTILLEJA Mutis.

Herbs, partially parasitic on the roots of other plants; leaves alternate; flowers red, yellow, purple or white, in dense, leafy-bracted spikes, the bracts usually colored and more conspicuous than the flowers; calyx flattened, 4-lobed and more deeply cleft above and below than on the sides; corolla flattened, 2-lobed, the upper lip arched and entire, the lower lip short and 3-lobed; stamens inclosed in the upper lip; capsule many-seeded.

1A. Lower lip of corolla at least one third as long as the upper (galea).
 1B. Leaves ovate-lanceolate with 2 or 3 pairs of lateral lobes .... 1. *C. parviflora*
 2B. Leaves linear to lanceolate, the lobes if present, linear.
  1C. Annual .... 2. *C. annua*
  2C. Perennial.
   1D. Calyx lobes distinct 3–8 mm. from apex, longer than the united part .... 3. *C. pallida*
   2D. Calyx lobes 0.5–2.5 mm. long, shorter than the united part.
    1E. Bracts violet-purple .... 4. *C. raupii*
    2E. Bracts yellow or yellowish.
     1F. Corolla 15–20 mm. long.
      1G. Stems 20–35 cm. tall .... 5. *C. yukonis*
      2G. Stems 7–12 cm. tall .... 6. *C. hyperborea*
     2F. Corolla 10–13 mm. long
      1G. Stem and inflorescence heavily villous... 7. *C. villosissima*
      2G. Stems puberulent or finely pubescent.... 8. *C. muelleri*
2A. Lower lip of corolla less than one-fifth the length of the galea.
 1B. Calyx lobes obtuse or rounded, bracts yellowish... 9. *C. unalaschcensis*

2B. Calyx lobes acute to acuminate, bracts red or dull yellowish.
  1C. Bracts all acute or acuminate....................10. *C. miniata*
  2C. Bracts partly or wholly obtuse or rounded.
    1D. Corolla 18–25 mm. long; inflorescence elongating ....11. *C. hyetophila*
    2D. Corolla 25–30 mm. long; inflorescence short and dense.................................12. *C. chryomactis*

1. *C. parviflora* Bong.

Stems glabrous, 1–4 dm. tall; leaves 2–4 cm. long, quite variable, but with from 2–6 dm. long linear or subulate teeth and a long pointed apex; bracts similar, reddish; flowers about 15 mm. long; calyx about 1 cm. long, pubescent, the lanceolate lobes about one-third as long as the tube; corolla tube about as long as the calyx; galea about 5 mm. long with a small tooth at the base of the apex and a pubescent ridge on the back.

Prince William Sound—Queen Charlotte I. Fig. 896.

2. *C. annua* Pennell.

Stems solitary, much branched, finely appressed-pubescent, villous in the inflorescence, about 5 dm. tall; leaves lanceolate, 3-ribbed, finely pubescent; bracts greenish-yellow, proximately becoming purple; calyx 12–13 mm. long; corolla 13–16 mm. long; galea 5–6 mm. long; lower lip 3–4 mm. long.

Tanana valley near Fairbanks.

3. *C. pallida* (L.) Spreng.

Leaves caudate; anterior lip of corolla about two-thirds the length of the galea; spikes relatively dense, the bracts overlapping and appressed. A circumpolar, polymorphic species represented in our region by 5 races as follows:

1A. Bracts yellowish, inflorescence merely hirsute.
  1B. Stems with spreading hairs, usually 2–5 dm. tall, the leaves pubescent..........................Subsp. *typica*
  2B. Stems usually appressed-pubescent, 1–3 dm. tall, leaves glabrate................................Subsp. *caudata*
2A. Inflorescence villous, bracts usually violet-purple (except in 1B.)
  1B. Corolla 20 mm. long; bracts and villous hairs of the inflorescence yellow..........................Subsp. *auricoma*
  2B. Corolla 14–18 mm. long; bracts purplish or ochroleuceous, hairs white.
    1C. Stems 1–3 dm. tall; leaves entire................Subsp. *mexiae*
    2C. Stems 5–15–25 cm. tall; leaves entire or some of them lobed..................................Subsp. *elegans*

The typical form is asiatic and occurs on the Bering Sea coast. Subsp. *caudata* Pennell has linear-attenuate or -caudate leaves 5–9 cm. long; corolla 15–20 mm. long. It ranges from Seward Pen. and Nunivak Island.—Mackenzie. Fig. 897. Subsp. *auricoma* Pennell has stems 15–20 cm. tall; leaves linear-lanceolate. 2–3 cm. long. Known from the Chandalar River. Subsp. *mexiae* (Eastw.) Pennell has linear-lanceolate leaves

4–6 cm. long, the bracts violet-purple. It is found from the Alaska Range and Matanuska to the Wrangell Mts. Subsp. *elegans* (Ostenf.) Pennell has linear or linear-lanceolate leaves 3–6 cm. long and violet-purple bracts. It occurs on Seward Pen. and the Arctic Coast to Hudson Bay.

4. *C. raupii* Pennell.

Stems several, 3–5 dm. tall, finely retrorse-pubescent; leaves linear, attenuate or caudate, 3–6 cm. long; bracts oval, becoming lanceolate, with a pair of lateral lobes; inflorescence villous; calyx 13–16 mm. long, cleft one-half its length, violet-purple; corolla 15–18 mm. long; galea 5–6 mm. long, acute, green, hirsute, with wide, glaborus, purplish margins; lower lip 2.5–3 mm. long.

Tanana Valley—Keewatin—James Bay—Peace River. Fig. 898.

5. *C. yukonis* Pennell.

Stems 20–35 cm. tall, purplish, pubescent with spreading or retrorse white hairs; inflorescence hirsute or villous with yellowish hairs; leaves linear, attenuate, 2–6 cm. long; bracts lanceolate with 1 or 2 pairs of short lateral lobes, obtuse or rounded, yellowish; calyx 13–18 mm. long, cleft three-fifths to two-thirds its length; galea 7–8 mm. long; lower lip 4–5 mm. long.

Yukon Territory.

6. *C. hyperborea* Pennell.

Stems from a much-branched crown, hirsute-pubescent; leaves lance-linear, attenuate, 2–4 cm. long, the lowest entire but most with 1 or 2 pairs of narrow lateral lobes; calyx 13–17 mm. long, cleft one-half its length; galea 5–8 mm. long, green with pale yellow margins; lower lip 3–4 mm. long.

Seward Pen.—central Yukon. Fig. 899.

7. *C. villosissima* Pennell.

Stems 5–14 cm. tall; leaves linear lanceolate, 1–4 cm. long, some of the upper ones with a pair of divaricate lobes; bracts ovate, with 1 or 2 pairs of lobes; obtuse or rounded, yellowish; calyx 10–13 mm. long, cleft about one-half length, its lobes very short; galea 5–6 mm. long; lower lip 3–4 mm. long.

Southwest Yukon. Fig. 900.

8. *C. muelleri* Pennell.

Stems several, 15–30 cm. tall, puberulent or finely pubescent, hirsute with yellowish hairs in the inflorescence; leaves linear, attenuate, entire, finely pubescent, 25–35 mm. long; bracts lanceolate or ovate-lanceolate, the lowest entire, the upper with a pair of slender lobes; calyx cleft two-fifths of its length, the lobes cleft only about 1.5 mm.; galea 5–6 mm. long; the lower lip 4–5 mm. long.

Southwest Yukon.

9. *C. unalaschcenis* (C. & S.) Malte.

Stems lanate-pubescent to glabrate, villous-hirsute in the inflorescence, 3–6 dm. tall; leaves entire, 5–10 cm. long, strongly 3-ribbed; bracts yellowish to orange, oval, 2–3 cm. long, entire or the upper ones with 1 or 2 pairs of teeth; calyx 18–22 mm. long, cleft one-half its length; corolla 2–3 cm. long. Subsp. *transnivalis* Pennell of northwest B. C. and Yukon is a smaller form with leaves lanceolate, 4–6 cm. long; corolla 15–20 mm. long.

Along the coast, Aleutian and Pribilof I.—southeast Alaska. Fig. 901.

10. *C. miniata* Dougl.

Stems 2–6 dm. tall glabrous nearly to the inflorescence; leaves lanceolate or linear, 3–6 cm. long, 3-nerved, glabrous; bracts crimson, often more or less cleft; calyx teeth lanceolate, acute, about 5 mm. long; corolla up to 30 mm. long; galea up to 15 mm. long; lower lip small.

Southeast Alaska—Alba.—Colo.—Utah—Ore. Fig. 902.

11. *C. hyetophila* Pennell.

Stems several, 3–6 dm. tall, glabrous or slightly pilose, villous-hirsute in the inflorescence; leaves linear-lanceolate or narrowly lanceolate, 3–10 cm. long, usually entire, 3-ribbed; bracts elliptic or oval the upper with a pair of lateral lobes, distally red; calyx 15–25 mm. long the teeth 3–7 mm. long; corolla 18–35 mm. long; galea 9–14 mm. long; lower lip 1–1.5 mm. long.

Southeast Alaska. Fig. 903.

12. *C. chrymactis* Pennell.

Stems several, erect, 3–5 dm. tall, glabrous or with sparse appressed hairs, villous in the inflorescence; leaves lanceolate, acuminate, 6–10 cm. long, entire, 3-ribbed; bracts mostly with 1–3 pairs of slender lobes; calyx 2–3 cm. long, the teeth 3–7 mm. long, red; corolla 25–30 mm. long; galea 11–15 mm. long; lower lip 1–2 mm. long.

Glacier and Yakutat Bays.

11. ORTHOCARPUS Nutt.

Alternate-leaved annuals related to *Castilleja;* leaves sessile, pectinately cleft or entire, those of the inflorescence sometimes highly colored; flowers perfect, in terminal spikes; calyx tubular or tubular-campanulate, 4-cleft; corolla very irregular, the upper lip erect and not exceeding the saccate, 3-lobed lower lip; capsula oblong; seeds many, reticulate. (Greek, erect fruit.)

O. hispidus Benth. Lesser Paintbrush.

Stems usually simple, 10–25 cm. tall, pubescent throughout; leaves 2–4 cm. long with linear-lanceolate lobes, the flowering leaves similar but shorter with more and stiffer lobes; flowers about 15 mm. long; calyx

lobes nearly as long as the tube, linear; corolla whitish or cream-colored, the upper lip sharp-pointed and seemingly longer than the 3-lobed lower lip.

Skagway, probably introduced from western U. S.

12. EUPHRASIA (Tourn.) L.

Erect, usually branching herbs partially parasitic on other plants; leaves opposite, dentate or incised; flowers in leafy, terminal spikes; calyx tubular, 4-cleft; corolla 2-lipped, the upper lip 2-lobed, the lower lip larger, with 3 spreading lobes; capsule oblong; seeds many, oblong, longitudinally ribbed. The species are known as Eyebright. (Greek, delight.)

Inflorescence nearly capitate............................1. *E. mollis*
Inflorescence more elongate............................2. *E. subarctica*

1. *E. mollis* (Ledeb.) Wettst.

Stems pubescent, 4–12 cm. tall; leaves 4–10 mm. long; inflorescence compact; calyx densely pilose, its triangular teeth barely acute. Closely related to *E. subarctica.*

East Asia, the Aleutians and southwest Alaska. Fig. 904.

2. *E. subarctica* Raup.

E. disjuncta of reports from Alaska and Yukon.

Stems finely puberulent, 6–30 cm. tall, often branched below; leaves 8–18 mm. long, ovate or orbicular, crenate with 7–11 teeth; bracts large and resembling the leaves but with more pointed teeth; corolla 4–5.5 mm. long and with a yellow eye; capsule 4–5 mm. long, about equaling the very acute calyx teeth.

Central and southwest Alaska—Lab.—Newf.—Maine—Alba. Fig. 905.

13. PEDICULARIS (Tourn.) L.

Annual, biennial or perennial herbs; leaves pinnate or pinnatifid; flowers perfect in terminal spikes or racemes; calyx cleft on the lower side, 2- to 5-lobed; corolla strongly 2-lipped; upper lip (galea) compressed, often beaked or toothed; lower lip 3-lobed, the lobes usually spreading; stamens ascending under the upper lip; capsule compressed and obliquely beaked. (Latin, louse.) The species are often known as Lousewort, but the Eskimo call the arctic species Bumble-bee Plant.

1A. Leaves verticillate.
  1B. Leaves deeply pinnatifid..........................12. *P. chamissonis*
  2B. Leaves 1- to 2-pinnately parted..................13. *P. verticillata*
2A. Leaves alternate (occasionally opposite).
  1B. Galea with a conical or thick-subulate beak.
    1C. Stem low more or less leafy.................... 7. *P. lapponica*
    2C. Stem scapiform (or with 1 pair of leaves)........ 8. *P. ornithorhyncha*
  2B. Galea with apex more or less incurved.
    1C. Annuals or biennials with branching stems.
      1D. Flowers yellowish........................... 9. *P. labradorica*

2D. Flowers purplish-red.
1E. Stems 25–75 cm. tall........................10. *P. parviflora*
2E. Stems less than 2 dm. tall..................11. *P. pennellii*
2C. Stems simple from perennial roots.
1D. Stems scapiform.
1E. Corolla yellow............................ 1. *P. capitata*
2E. Corolla purplish.......................... 2. *P. sudetica*
2D. Stems leafy.
1E. Corolla yellowish.
1F. Corollas about 12 mm. long................. 3. *P. flammea*
2F. Corolla 15–20 mm. long.................. 4. *P. oederi*
2E. Corolla rose to purplish.
1F. Spike densely lanate...................... 5. *P. lanata*
2F. Spike pubescent but not densely lanate.
1G. Stems scape-like with 1–3 leaves........ 2. *P. sudetica*
2G. Stems more leafy........................ 6. *P. langsdorfii*

1. *P. capitata* Adams.

Stems usually pubescent, 3–12 cm. tall; leaves few, slender-petioled, the pinnate divisions deeply cut or toothed; flowers 2–6 in a capitata cluster; calyx 5-lobed, the lobes crenate; corolla up to 35 mm. long.
Bering Sea—Ellesmereland—Hudson Bay—Aleutians. Fig. 906.

2. *P. sudetica* Willd.

Stems solitary or few, glabrate but villous in the inflorescence, 15–40 cm. tall, scape-like but with a few leaves; base leaves lanceolate in outline and long-pointed; flowers in dense spikes which become elongated in fruit; calyx villous; corolla 15–22 mm. long, the galea recurved, 6–7 mm. long.
Eurasia — all of Alaska — Ellesmereland — James Bay — Mackenzie. Fig. 907.

3. *P. flammaea* L.

Stems glabrous or slightly woolly, 4–10 cm. tall; leaves few, 2–6 cm. long, pinnately divided into oblong or oval crenate divisions; calyx with 5 lanceolate teeth; corolla tube and lower lip yellowish, the galea tinged purple or crimson and about 6 mm. long.
A specimen from Goodnews Bay seems to belong here but the main range is east of our area. Fig. 908.

4. *P. oederi* Vahl.

Stems 6–20 cm. tall; leaves 3–7 cm. long, pinnately divided into dentate segments 3–5 mm. long; spikes 3–10 cm. long; calyx lobes lanceolate and more or less ciliate on the margins; corolla 18–22 mm. long, yellowish with purple-tinged galea about 8 mm. long and boat-shaped; lower lip deeply cleft with rounded lobes.
Eurasia—Kotzebue—Yukon—Mont.—Aleutians. Fig. 909.

5. *P. lanata* Willd.

Whole plant woolly except the lower leaves which are glabrous; leaves 2–6 cm. long, the divisions up to 6 mm. long with crenate to pin-

natifid margins; spikes in fruit usually much longer than the remainder of the stem, often more than 2 dm. long; corolla rose-purple, about 2 cm. long.

Eurasia—Arctic Alaska—Ellesmereland—Greenland—Lab.—B. C.—Aleutians. Fig. 910.

6. *P. langsdorfii* Fisch.
P. arctica R.Br.

Stems 4–18 cm. tall; leaves pinnatifid, the segments ovate with crenate margins, 1–3 mm. long; spikes dense, 3–5 cm. long; calyx about 8 mm. long, woolly, the lobes lanceolate with hairy margins; corolla 20–25 mm. long; galea 10–14 mm. long with a small tooth near the apex. The plant of the arctic is more pubescent in the inflorescence and has somewhat smaller flowers.

East Asia—Arctic Coast and central Alaska—Kodiak—Aleutians. Fig. 911.

7. *P. lapponica* L.

Stems usually simple, leafy, 10–25 cm. tall; leaves lanceolate, up to 35 mm. long, pinnately incised into oblong, serrate lobes; spikes short and dense, almost capitate; flowers light yellow, 12–14 mm. long, the galea erect and arched.

Rare in our area, Eurasia—Baffin Land—Greenland—Mackenzie. Fig. 912.

8. *P. ornithorhyncha* Benth.
P. pedicellata Bunge.

Stems 1–2 dm. tall, appearing scapose but usually with one pair of leaves; basal leaves long-petioled, pinnatifid almost to the midrib, the pinnae again pinnatifid, the teeth acute; galea deeply bent, the outside measuring almost 1 cm. long.

Southeast Alaska—Wash. Fig. 913.

9. *P. labradorica* Panzer.
P. euphrasioides Steph.

Stems hirsute, usually much branched, 1–4 dm. tall; lower leaves pinnatifid, the upper merely crenate, 2–4 cm. long; flowers in axils of upper leaves or spicate, about 15 mm. long, yellow or sometimes the galea tinged reddish-purple; galea short with a very short beak and 2 lanceolate teeth at lower side of apex; pod 2 times as long as the calyx.

Asia—nearly all of Alaska—Greenland—Lab.—B. C. Fig. 914.

10. *P. parviflora* Smith.

Stems usually glabrous and branched, 3–9 dm. tall; stem leaves deeply pinnatifid, the segments crenately toothed, the uppermost reduced; flowers solitary in the upper axils or in loose terminal spikes,

10–13 mm. long; galea boat-shaped, 3–5 mm. long; calyx 2-cleft.
Central and south Alaska—Hudson Bay—Lake Mistassini—Ore. Fig. 915.

11. *P. pennellii* Hult.

Stem glabrous, widely branched from the base, 10–15 cm. tall; leaves pinnatisect, the segments toothed; calyx glabrous, 2-parted, the teeth dentate; corolla rose-purple, 10–14 mm. long; galea erect with 2 acute teeth well back from the apex.
Alaska Pen.—Kotzebue—Lake Illiamna. Fig. 916.

12. *P. chamissonis* Stev.

Robust perennial 2–6 dm. tall; leaves usually in whorls of 3 or 4, up to 9 cm. long, deeply pinnatifid, the lanceolate divisions serrate or incised; corolla reddish, up to 25 mm. long; galea boat-shaped, scarcely as long as the lower lip.
East Asia—Aleutians—Alaska Pen.—Pribilof I. Fig. 917.

13. *P. verticillata* L.

Stems somewhat pubescent, usually clustered, 1–4 dm. tall; basal leaves long-petioled, those of the stem verticillate and short-petioled or sessile; flowers in spikes, a few in the axils of the upper leaves; galea about 5 mm. long.
Eurasia through Alaska and Yukon. Fig. 918.

Pedicularis groenlandica Retz. The Little Elephants has been reported from Alaska. It is characterized by the galea which is much prolonged into a narrow recurved beak.

14. RHINANTHUS L.

Annual, erect, mostly branching herbs with opposite leaves; flowers perfect, solitary in the axils of the upper leaves, becoming 1-sided spikes; calyx compressed, 4-toothed, becoming inflated in fruit, reticulate; corolla 2-lipped, the upper compressed, with 2 minute teeth below the apex, the lower lip shorter with 3 lobes; anthers hairy, the sacs distinct; capsule orbicular, flat, dehiscent, containing several winged seeds. (Greek, nose-flower, from the beaked corolla.)

R. minor L. subsp. *groenlandicus* (Chab.) Neum. Rattlebox.
R. borealis Sternb. *R. crista-galli* C. & S.

Stems glabrous or pubescent above, 1–7 dm. tall; leaves lanceolate or oblong-lanceolate, becoming broader at the base and more pointed on the upper part of the stem, scabrous; calyx short-hairy, ciliate on the margins; corolla yellow; fruiting calyx 1 cm. or more broad.
Aleutians—Talkeetna—Yukon—Greenland—N. H.—Conn.—N. M.—Ore. Fig. 919.

50. LENTIBULARIACEAE (Bladder-wort Family)

Small scapose herbs growing in water or wet places; leaves, when submerged, dissected into filiform segments and in our species bladder-bearing; flowers perfect; calyx of 2 or 5 sepals; corolla 2-lipped, the tube spurred or saccate; stamens 2; ovary 1-celled with central placenta; style short or none.

Plants of wet places with entire leaves.................. 1. *Pinguicula*
Submerged plants with dissected leaves................. 2. *Utricularia*

1. PINGUICULA (Tourn.) L.

Perennials of wet places with 1-flowered scapes; leaves in rosettes, thick, producing a musilagenous secretion to which insects adhere; corolla in our species blue to purple, the tube produced into a nectar-bearing spur. (Pinguis, fat, in allusion to the greasy leaves.)

Scape villous; corolla less than 10 mm. long..............1. *P. villosa*
Scape smooth, corolla 12–25 mm. long.....................2. *P. vulgaris*

1. *P. villosa* L. Hairy Butterwort.

Scapes finely villous, 3–8 cm. tall; leaves 3–5, 6–12 mm. long; flowers 3–5 mm. broad; corolla with the upper lip 2-parted, the lower lip 3-parted, the tube contracted into a straight spur 3–5 mm. long. Grows in sphagnum bogs and is very hard to detect except when in flower.

Circumpolar, south to Unalaska, Prince William Sound, southeast Alaska, Lab. Fig. 920.

2. *P. vulgaris* L. Bog Violet. Common Butterwort.

Scapes glabrous or nearly so, 3–20 cm. tall; leaves 3–7 ovate to elliptic, 15–40 mm. long; lips of the corolla equally spreading, the upper 2-lobed, the lower 3-lobed; spur subulate, acute.

Circumpolar, south to Aleutians—Wash.—Mont.—Mich.—N. Y. Fig. 921.

2. UTRICULARIA L.

Aquatic plants with immersed, finely-dissected, bladder-bearing leaves; bladders small, urn-shaped and provided with valvular lids, small aquatic animals thus being entrapped and digested; sepals 2; corolla yellow or yellowish with spur at the base. (Utriculus, a little bladder.)

1A. Leaf segments flat.....................................2. *U. intermedia*
2A. Leaf segments filiform.
  1B. Leaves 2–5 cm. long................................1. *U. macrorhiza*
  2B. Leaves less than 1 cm. long........................3. *U. minor*

1. *U. macrorhiza* LeConte. Common Bladderwort.
U. vulgaris Auct.

Stems submerged and very leafy; leaves 2- to 3-pinnately dissected; bladders 2–4 mm. long; scapes 1–3 dm. long, 5- to 10-flowered; spur horn-

like, slightly curved; corolla bright yellow; pedicels recurved in fruit. Often included in the European *U. vulgaris* but differs in several respects.

All our area except the Arctic—Fla.—Mo.—Okla.—Lower Calif. Fig. 922.

2. *U. intermedia* Hayne. Flat-leaved Bladderwort.

Leaves 5–15 mm. long, trichotomous at the base; bladders on separate, leaflets branches; scapes 1- to 4-flowered; corolla yellow, the spur acute and appressed to the lower lip and nearly as long; fruiting pedicels erect. Commonly propagates by velvety winter buds.

Infrequent, circumboreal south to N. J.—Ind.—Calif. Fig. 923.

3. *U. minor* L. Lesser Bladderwort.

Stems slender with scattered alternate leaves; bladders not abundant, 2 mm. long; scapes 5–15 cm. long, 1- to 10-flowered; corolla pale yellowish, the upper lip very small; spur short and blunt; pedicels recurved in fruit.

Infrequent, circumpolar south to Conn.—Penn.—Ind.—Colo.—Calif. Fig. 924.

51. OROBANCACEAE (Broom-rape Family)

A family of root-parasites without green foliage; leaves reduced to appressed scales; flowers perfect, sessile in the axils of the scales or solitary on peduncles in the axils of the scales; calyx 4- to 5-toothed, corolla much as in *Scrophulariaceae;* ovary 1-celled with 2–4 parietal placentae; seeds numerous, reticulated, wrinkled or striate.

Glabrous, thick, fleshy, brownish-red plant ....1. *Boschniakia*
Plants glandular-pubescent and more slender ....2. *Orobanche*

1. BOSCHNIAKIA C. A. Mey.

Stems thick and fleshy with numerous flowers in a cone-like spike; the whole plant of a reddish color; base of the anthers rounded. (Boschniak was a Russian botanist.)

B. rossica (C. & S.) B. Fetsch. Poque.
B. glabra C. A. Mey.

Stems 10–35 cm. tall from tuber-like formations parasitically attached to the roots of *Alnus;* lower scales triangular and sharp-pointed, broadest at the base, the upper blunt and broadest near the middle, often ciliate on the edges, otherwise glabrous; corolla 10–15 mm. long.

Asia—Seward Pen.—Mackenzie—Vancouver I. Fig. 925.

2. OROBANCHE (Tourn.) L.

Glandular or viscid-pubescent herbs parasitic on the roots of various plants; flowers long-peduncled; calyx campanulate with acute or acum-

inate lobes; corolla oblique, the tube elongated and curved, the upper lip 2-lobed, the lower lip 3-lobed. (Greek, choke-vetch.)

Stems 1–2 cm. long....................................1. *O. uniflora*
Stems 4–10 cm. long....................................2. *O. fasciculata*

1. *O. uniflora* L. One-flowered Cancer-root.
Aphyllon uniflorum T. & G. *Thalesia uniflora* (L.) Britt.

Stems very short and nearly subterranean, bearing 1–4 peduncles 5–20 cm. tall; corolla tinged violet, 15–20 cm. long, puberulent.

Sand Point and Kodiak; B. C.—Newf.—S. C.—Texas. Fig. 926.

2. *O. fasciculata* Nutt. Clustered Cancer-root.

Aphyllon fasciculatum Gray. *Thalesia fasciculata* (Nutt.) Britt.

Stems rising 2–8 cm. above the surface, densely glandular-pubescent; peduncles few to several, 2–10 cm. long; corolla yellowish or purplish, 15–25 mm. long.

Yukon—Ind.—Neb.—Calif. Fig. 927.

52. PLANTAGINACEAE (Plantain Family)

Annual or perennial herbs, mostly with basal leaves; flowers subtended by bracts, usually in dense spikes; calyx 4-parted, inferior; corolla campanulate or tubular with 4 lobes, scarious, nerveless, persistent; pistils 1; ovary superior, 1- to 4-celled; stamens 2 or 4; fruit usually a circumsissle capsule.

PLANTAGO (Tourn.) L.

Our species are acaulescent herbs with strongly ribbed or fleshy leaves and flowers in dense spikes on rather long peduncles. (The Latin name.)

1A. Leaves linear.
  1B. Bracts linear, much longer than the calyx.........2. *P. aristata*
  2B. Bracts ovate or orbicular, about the same length as the calyx....................................1. *P. maritima*
2A. Leaves wider.
  1B. Leaves ovate, abruptly contracted at base.........3. *P. major*
  2B. Leaves lanceolate to ovate, sometimes narrowly so.
    1C. Capsule indehiscent............................4. *P. macrocarpa*
    2C. Capsule a circumsissle pyxis.
      1D. Seed concave on the inner surface...........5. *P. lanceolata*
      2D. Seed nearly flat on the inner surface.
        1E. Plant sparingly pubescent with brown wool at the base............................6. *P. eriopoda*
        2E. Plant somewhat villous with little or no wool at base..........................7. *P. canescens*

1. *P. maritima* L. subsp. *juncoides* (Lam.) Hult. Goose-tongue.

A seaside perennial with fleshy, linear leaves; scapes either longer or shorter than the leaves, pubescent, especially just below the spike; spikes dense, blunt, 3–10 cm. long; corolla pubescent within, the lobes spreading; capsule 2–3 mm. long, 2- to 3-seeded.

Along the coasts this species is widespread in temperate climates. Fig. 928.

2. *P. aristata* Michx. Large-bracted Plantain.

Annual, dark green; scapes erect, 12–35 cm. tall; leaves linear, acuminate, entire, narrowed into slender petioles, 3–8 mm. wide; spikes dense, cylindric, 2–15 cm. long; bracts linear, up to 3 cm. long; pyxis 2-seeded, the seed concave on the face.

Dawson, probably adventative from central U.S.A.

3. *P. major* L. Common Plantain.

A weed with somewhat pubescent, oval or ovate leaves 5–15 cm. long on petioles of same length or less, 5- to 7-ribbed; scapes 1–5 (–7) dm. tall; spikes 4–20 cm. long; pyxis ovoid, about 3 mm. long. Reports of *P. asiatica* from Alaska refer to a form of this species.

Generally distributed in settled parts of our region and of wide geographic distribution. Fig. 929.

4. *P. macrocarpa* C. & S. Seashore Plantain.

Leaves mostly 5- to 7-nerved on dilated petioles; scapes equaling or exceeding the leaves; spikes 2–5 cm. long; bracts fleshy and very dark-colored and with scarious margins; capsule ovoid-oblong, 6–8 mm. long; seeds 2, hollowed on the face.

Commander and Aleutian I. along the coast to Wash. Fig. 930.

5. *P. lanceolata* L. Ribgrass. Buckhorn.

More or less pubescent; leaves 3- to 5-nerved, usually on long petioles and with a tuft of hairs at the base; scapes much exceeding the leaves, up to 6 dm. long; spikes dense, cylindrical, 2–8 cm. long; sepals broadly scarious-margined with green midrib.

Native of Europe but widely introduced in temperate regions.

6. *P. eriopoda* Torr. Saline Plantain.

Perennial; leaves narrowly lanceolate or oblanceolate, entire somewhat pubescent, up to 2 dm. long; scapes 15–40 cm. tall; spikes up to 15 cm. long at maturity, sparse below but dense above; sepals oblong-ovate, with wide scarious margins.

Yukon—Mackenzie—Keewatin—Neb.—N. M.—Calif.

7. *P. canescens* Adams
P. septata Morris.

Perennial; leaves lanceolate to oblanceolate, 5-ribbed, with long or short petioles, entire or remotely dentate, the blade up to 15 cm. long and 3 cm. wide but often quite small, more or less pubescent; scapes 1–5 dm. tall; spikes up to 9 cm. long, dense; pyxis very finely reticulated.

Asia, central Alaska—Mackenzie and Mont. Fig. 931.

53. RUBIACEAE (Madder Family)

Our species all herbaceous plants; leaves opposite or whorled, entire; flowers perfect but often dimorphous or trimorphous; ovary inferior, 2- to 4-celled; stamens as many as the lobes of the corolla and alternate with them; fruit in our species of two 1-seeded carpels.

GALIUM L.

Annual or perennial herbs with 4-angled stems and whorled leaves; flowers small, mostly white, in cymes or panicles; calyx obsolete; corolla rotate; stamens mostly 4; styles 2; fruit separating at maturity into 2 indehiscent carpels. (Greek, milk, which some species were used to curdle.)

1A. Fruit bristly.
  1B. Flowers in terminal panicles......................1. *G. boreale*
  2B. Flowers solitary or in 3's.
    1C. Stem leaves in 4's, wide........................2. *G. kamtschaticum*
    2C. Stem leaves in 6's to 8's.
      1D. Annual, leaves narrow, 3–7 cm. long...........3. *G. aparine*
      2D. Perennial, leaves wider, 1–3 cm. long.........4. *G. triflorum*
2A. Fruit smooth.
  1B. Leaves mostly in 5's (or 6's)......................6. *G. trifidum columbianum*
  2B. Leaves in 4's.
    1C. Pedicels long, thin, retrorsely scabrous.........6. *G. trifidum*
    2C. Pedicels short, thick, glabrous...................5. *G. brandgei*

1. *G. boreale* L. Northern Bedstraw.

Erect perennial, 2–6 dm. tall; leaves 3-nerved, lanceolate, in whorls of 4; sometimes the leaves may be almost linear or there may be fascicles of leaves in the axils; flowers in a large terminal panicle and very ornamental; fruit about 2 mm. in diameter.

Common except in the arctic; circumboreal, south to N. J.—Ind.—Mo.—N. M.—Calif. Fig. 932.

2. *G. kamtschaticum* Steller. Northern Wild Liquorice

Stems weak, 1–3 dm. tall; leaves broadly oval, orbicular or obovate, 3-nerved, obtuse, mucronulate, 10–30 mm. by 7–20 mm., sometimes ciliate; flowers terminal in 3's.

Asia—Aleutians—southeast Alaska—Wash. and in Que.—N. Y. Fig. 933.

3. *G. aparine* L. Cleavers.

Stems weak, prostrate or scrambling over other vegetation, 3–15 dm. long, hispid on the angles; leaves linear-oblanceolate, 30–70 mm. by 2–5 mm., rough on the midrib and margins; fruit about 4 mm. in diameter.

Aleutians—southeast Alaska; of very wide distribution. Fig. 934.

4. *G. triflorum* Michx. Sweet-scented Bedstraw.

Stems diffuse, glabrous or nearly so, shining, 3–10 dm. long; leaves in 6's, 2–6 cm. long, 3–12 mm. wide; peduncles often exceeding the

leaves, 1- to 5-flowered but mostly 3-flowered; fruit long-hispid with hooked hairs, about 3 mm. broad.

Aleutians—central Alaska—Greenland and circumboreal south to Fla.—La.—Texas—Calif. Fig. 935.

5. *G. brandegei* Gray. Brandege Bedstraw.

Forming dense, low, leafy mats, mostly glabrous; leaves small, broadly spatulate, less than 10 mm. long and equaling or exceeding the internodes; flowers lateral, solitary; pedicels short, stout, glabrous, often not exceeding the fruit in length. Closely related to the next species.

Seward Pen.—Lab.—Iceland—Maine—Great Lakes—N. M.—Calif.

6. *G. trifidum* L. Small Bedstraw.

Stems slender, diffuse and weak, retrorsely hispid; leaves narrowly linear to broadly spatulate, 4–10 mm. long; flowers minute; pedicels slender, solitary or terminal in 3's, scabrous, long and curved; fruit glabrous, its carpels about 1.5 mm. thick. Subsp. *columbianum* (Rydb.) Hult. is less diffuse; the stems ascending, 2–4 dm. long; leaves of the stem usually in 5's, those of the branches in 4's, 5–15 mm. long.

Aleutians—Mackenzie—Maine—N. Y.—Ind.—Colo. the subsp. in the coastal sections. Whole species circumboreal. Fig. 936.

54. CAPRIFOLIACEAE (Honeysuckle Family)

Shrubs, trees, vines or perennial herbs; leaves opposite; flowers perfect; calyx adnate to the ovary, its limb 3- to 5-parted; corolla gamopetalous, from rotate to tubular, often gibbous at the base, its limb 5-lobed and often 2-lipped; fruit a 1-seeded pod or more often a berry.

1A. Stamens 4; herbaceous trailing evergreen..........1. *Linnaea*
2A. Stamens 5, adnate to the corolla and alternate with its lobes; shrubs.
  1B. Corolla tubular; stigma capitate.
    1C. Corolla irregular..............................2. *Lonicera*
    2C. Corolla regular................................3. *Symphoricarpus*
  2B. Corolla rotate or nearly so.
    1C. Leaves pinnate................................4. *Sambucus*
    2C. Leaves simple.................................5. *Viburnum*

1. LINNAEA (Gronov.) L.

Slender, trailing evergreens, somewhat woody, with ascending branches; flowers fragrant, pinkish, borne on slender, drooping pedicels at the forked top of the erect peduncles; calyx 5-lobed; corolla bell-shaped to funnelform, 5-lobed; fruit 1-seeded. (Named for Linneus, the father of modern botany.)

L. borealis L. Twin-flower.

Leaves somewhat coriaceous, the blades oval or orbicular, generally crenate above the middle; peduncles at the fork and just below each flower with 2 glandular scales. Represented in our area by 3 forms.

The typical form with rounded leaf-apex and campanulate corolla in central Alaska and westward. Subsp. *americana* (Forbes) Hult. found from the Bering Sea across the continent has a longer, more trumpet-shaped corolla. Subsp. *longiflora* (Torr.) Hult. found in southeast Alaska—Idaho—Calif. has long, narrow sepals; a long narrow corolla; elliptical leaves which are acutish at the tip.

Whole species is circumboreal. Fig. 937.

2. LONICERA L.

Erect or climbing shrubs; leaves opposite, entire; corolla tubular, funnelform or campanulate, often gibbous at the base; fruit a few-seeded berry. (Adam Lonitzer was a German botanist.)

A vine with flowers in heads..........................1. *L. glaucescens*
A shrub with flowers in pairs on axillary peduncles......2. *L. involucrata*

1. *L. glaucescens* Rydb. Glaucous Honeysuckle.

Stems twining, glabrous; leaves glabrous above; glaucous and more or less pubescent below, ovate 2–8 cm. long, the upper pair connate-perfoliate; corolla yellow, changing to reddish, 20–25 mm. long, gibbous at the base.

Liard River Hot Springs—Mackenzie—Penn.—N. C.—Ohio.—Okla.

2. *L. involucrata* (Rich.) Banks. Black Twinberry.

A shrub with 4-angled twigs, 1–3 m. tall; leaves pubescent, at least on the veins and margins; corolla nearly regular, 10–12 mm. long, strongly gibbous at the base; fruit black with dark red involucre.

Southeast Alaska—Que.—Penn.—Ky.—Mont.—Calif. Fig. 938.

3. SYMPHORICARPUS (Dill.) Ludwig.

Shrubs; leaves simple, opposite, short-petioled; flowers perfect, white or pink; corolla campanulate; stamens 4 or 5, inserted on the corolla; ovary 4-celled; fruit a 2-seeded berry. (Greek, borne together, from the clustered fruit.)

S. rivularis Suksd. Snowberry.

Erect or diffuse shrub 3–12 dm. tall; leaves ovate to oblong, obtuse at each end, often whitish or pubescent beneath, 15–50 mm. long; flowers in small axillary clusters; corolla bearded within, about 6 mm. long; berry snow-white, 5–10 mm. in diameter. Probably only a subspecies of *S. albus* (L.) Blake.

Southeast Alaska—Que.—Va.—Colo. Fig. 939.

4. SAMBUCUS (Tourn.) L.

Shrubs growing in clumps; leaves odd-pinnate, the leaflets finely serrate; flowers small, whitish, in compound cymes; corolla rotate or saucer-shaped with the 5 stamens inserted at its base; berry-like drupe 3- to 5-celled and -seeded. (The Latin name of the elder.)

S. racemosa L. subsp. *pubens* (Michx.) Hult. Red-berried Elder.

A shrub 1–4 m. tall with pyramidal inflorescence of whitish flowers which turn brown in drying; cyme 5–8 cm. by 4–6 cm.; drupe scarlet, occasionally orange.

Common in the Pacific coast regions, central Alaska—Newf.—Ga.—Colo.—Calif. Fig. 940.

5. VIBURNUM (Tourn.) L.

Shrubs or small trees; leaves simple; flowers white with spreading 5-lobed corolla; stamens 5, the style short and 3-cleft; ovary 1- to 3-celled but the fruit with a single compressed seed. (Ancient Latin name.)

V. edule (Michx.) Raf. Few-flowered Highbush Cranberry.
V. pauciflorum Pylaie

10–25 dm. tall; leaves variable, more or less pubescent beneath and usually 2 glands at the base of the blade; cymes rather few-flowered, short-rayed; drupe 8–10 mm. long, the stone flat.

Seward Pen.—Mackenzie—Newf.—Penn.—Colo.—Wash. Fig. 941.

55. ADOXACEAE (Moschatel Family)

A glabrous perennial with scaly or tuberiferous rootstock; basal leaves ternately divided; flowers small, greenish, borne in a terminal capitate cluster; corolla rotate, 4- to 6-lobed; stamens twice as many as the lobes of the corolla, borne in pairs on its tube; anthers peltate, 1-celled; ovary 3- to 5-celled; ovules 1 in each cell; fruit a small drupe with 3–5 nutlets.

ADOXA L.

The only genus. (Greek, without glory, i.e. insignificant.)

A. moschatellina L. Moschatel. Musk Root.

Stems simple, weak, 6–15 cm. tall, bearing a pair of ternate leaves; heads few-flowered, 6–8 mm. in diameter; drupes green, bearing the persistent calyx-lobes.

Circumpolar, south to Wis.—Iowa—Colo. Fig. 942.

56. VALERIANACEAE (Valerian Family)

Herbs with opposite, entire or pinnately divided leaves and no stipules; flowers small, in cymes; calyx tube adnate to the ovary, its limb inconspicuous in flower but often pappus-like in fruit; corolla tubular, funnelform or salver-shaped with 3–5 lobes, sometimes gibbous or spurred at the base; stamens 1–4, exerted; ovary 3-celled, only one maturing, giving rise to a 1-seeded fruit.

VALERIANA (Tourn.) L.

Heavy-scented perennials with small whitish or pinkish flowers in

close cymes; calyx-limb at first inrolled, developing into 5–15 plumose bristles in fruit; corolla funnelform or salver-shaped, 5-lobed, often saccate at the base; stamens 3; achene flattened, 1-nerved on one side, 3-nerved on the other side. (Latin, valere, to be strong.)

1A. Corolla of pistillate flowers 2–3 mm. long............1. *V. septentrionalis*
2A. Corolla of pistillate flowers 5–8 mm. long.
  1B. Upper stem leaves all 3- to 7-foliate............3. *V. sitchensis*
  2B. Upper stem leaves simple or 3-foliate............2. *V. capitata*

1. *V. septentrionalis* Rydb. Northern Valerian.

Stems erect, 2–4 dm. tall, glabrous or the inflorescence minutely pubescent; stem leaves usually 3-pairs with 5–7 segments, the segments oval to linear-lanceolate; flowers white, about 3 mm. wide.

Atlin—Great Bear Lake—Hudson Bay—Newf.—Wyo.

2. *V. capitata* Pall. Capitate Valerian.

Stems glabrous, slender, 2–6 dm. tall; flowers in a capitate cluster which elongates in fruit; lower leaves simple, the upper trifoliate or 3-lobed, the center part much wider than the lateral.

Common, Eurasia across Alaska and Yukon to Mackenzie. Fig. 943.

3. *V. sitchensis* Bong. Sitka Valerian.

Stems glabrous except in the inflorescence, 4–8 dm. tall; stem leaves 3- to 5-foliate, the lower less divided or simple; leaflets coarsely toothed; inflorescence rather dense; corolla white or pinkish, 6 mm. long.

Mountain meadows, Talkeetna Mts.—southeast Alaska—Mont.—Idaho—Ore. Fig. 944.

57. CAMPANULACEAE (Bellflower Family)

Our species all perennial (or biennial) caulescent herbs; leaves simple, alternate; calyx entirely enclosing the 2- to 5-celled ovary; flowers perfect; corolla 5-lobed, blue or rarely white; stamens 5, inserted with the corolla at the line where the calyx becomes free from the ovary; fruit a 2- to 5-celled capsule; seeds numerous.

Corolla regular..1. *Campanula*
Corolla 2-lipped..2. *Lobelia*

1. CAMPANULA (Tourn.) L.

Calyx 5-cleft; capsules opening by pores usually formed by the uplifting of small lids. (Diminutive of Latin, campana, a bell.)

1A. Calyx with deflexed appendages in the sinuses.......1. *C. dasyantha*
2A. Calyx without appendages at the sinuses.
  1B. Corolla rotate, lobed almost to the base...........2. *C. aurita*
  2B. Corolla campanulate, lobes not longer than the tube.
    1C. Calyx pubescent.
      1D. Calyx lobes laciniate..........................4. *C. lasiocarpa*
      2D. Calyx lobes entire..............................3. *C. uniflora*
    2C. Calyx glabrous.
      1D. Style much exceeding the corolla...........5. *C. scouleri*
      2D. Style shorter than the corolla..................6. *C. rotundifolia*

1. C. *dasyantha* Bieb.

Stems 3–10 cm. tall, 1-flowered; leaves mostly basal, ovate to ovate-spatulate, crenate with gland-tipped teeth, the stem leaves varying to lanceolate or linear; calyx lobes triangular-lanceolate, about 1 cm. long; corolla deep blue, 25–35 mm. long, the tube longer than the lobes.
Japan—Aleutians. Fig. 945.

2. C. *aurita* Greene.

Stems erect or ascending, often tufted, 1- to 3-flowered, 7–25 cm. tall; leaves oblong to linear, sessile by a narrow base, the lower ciliate on the margin near the base, entire or with a few teeth; calyx teeth lanceolate, usually with a pair of acute lobes near the base; corolla spreading, 10–15 mm. long.
Yukon valley—Mackenzie. Fig. 946.

3. C. *uniflora* L. Arctic Harebell.

Stems 5–15 cm. tall, glabrous or nearly so; lower and basal leaves spatulate, narrowed into a petiole; upper leaves narrower; flowers erect or ascending, pubescent at the base of the calyx; loves of the corolla about equaling the tube; capsule ascending, opening by pores near the summit.
Aleutians—Arctic, circumpolar, to Colo. Fig. 947.

4. C. *lasiocarpa* Cham. Mountain Harebell.

Stems 3–15 cm. tall, the alpine form usually 1-flowered, the lowland form branched; lower leaves glabrous or somewhat ciliate, upper leaves more ciliate; hypanthium villous; sepals 6–10 mm. long and lobed; corolla 15–25 mm. long. This is our most widely distributed and common species.
Throughout our areas except the high Arctic. Asia—Alba.—B. C. Fig. 948.

5. C. *scouleri* Hook. Scouler Harebell.

Glabrous or slightly pubescent; stems slender, clustered from branching rootstocks, 1–3 dm. long; lower leaves ovate, acute, remotely serrate, 2–3 cm. long; upper leaves narrowed to linear bracts; flowers nodding; calyx lobes twice as long as the tube; corolla pale or white, the acute reflexed lobes nearly equaling the tube.
Wrangel—Calif.

6. C. *rotundifolia* L. Harebell. Blue Bells of Scotland.

Perennial by slender rootstocks; stems 15–50 cm. tall; basal leaves nearly orbicular to cordate, usually dentate, 6–25 mm. long, often wanting at flowering time; upper leaves narrower, often linear; flowers drooping or spreading; corolla 15–25 mm. long; capsule pendulous, ribbed, opening by valves at the base. This is a very diverse group

from which several species have been described; the typical form is near to or identical with the form known by some as *C. petiolata* DC. which has linear or subulate lobes of the corolla; narrow linear upper leaves and usually branching stem. The latest to be described is *C. latisepala* Hult. which has usually only 1 but may have up to 3 flowers with triangular calyx lobes 2–3 mm. wide at the base and up to 12 mm. long; the upper leaves relatively wide. This form connects through the variety *dubia* Hult. which has narrower upper leaves and sepals and numerous other variations with the typical form of the species. Var. *alaskana* Gray and *C. heterodoxa* are other names used in this group.

Circumboreal, south to N. J.—Ind.—Neb.—N. M.—Calif. Fig. 949.

2. LOBELIA (Plum.) L.

Corolla split nearly to the base on the upper side; upper 2 lobes narrow, spreading or reflexed; lower 3 lobes united into a broad lip; stamens 5, the filaments monodelphous, the anthers united, two or all bearded at the apex; capsule 2-valved.

L. kalmii L.

Biennial; stems slender, 15–35 cm. tall, simple or with a few branches; basal leaves spatulate or oblanceolate, the stem leaves narrower, varying to linear, up to 4 cm. long; sepals acute, about 3 mm. long; corolla 7–8 mm. long.

Liard River Hot Springs — Great Slave Lake — Man. — N. D. — Mont.—Wash. Fig. 950.

PLATE XXXVI

Scale in millimeters.

FIG.

839. *Swertia perennis* L. Flower, leaf and nectiferous pit.
840. *Lomatigonium rotatum* (L.) Fries. Flower and pair of leaves.
841. *Gentiana prostrata* Haenke. Two joints of stem and flower.
842. *Gentiana douglasiana* Bong. Portion of corolla laid open and leaf.
843. *Gentiana algida* Pall. Leaf and flower.
844. *Gentiana glauca* Pall. Portion of corolla, leaf and seeds.
845. *Gentiana platypetala* Griseb. Flower and pair of leaves.
846. *Gentiana barbata* Froel. Flower and basal leaf.
847. *Gentiana tenella* Rottb. Flower and two lobes of corolla.
848. *Gentiana auriculata* Pall. Flower and lower stem leaf.
849. *Gentiana acuta* var. *plebeja* Corolla laid open and lower stem leaf
850. *Gentiana aleutica* C. & S. Flower and leaf.
851. *Gentiana propinqua* Rich. Flower and leaf.
852. *Menyanthes trifoliata* L. Leaf and flower.
853. *Fauria cristi-galli* (Menz.) Mikano. Leaf, flower and fruit.
854. *Apocyanum androsaemifolium* L. Flower, leaf and fruit.
855. *Polemonium acutiflorum* Willd. Flower and section of leaf.
856. *Polemonium pulcherrimum* Hook. Flower and section of leaf.
857. *Polemonium boreale* Adams. Flower and tip of leaf.
858. *Phlox sibirica* L. Flower and leaf.
859. *Collomia linearis* Nutt. Flower and leaves.
860. *Romanzoffia sitchensis* Bong. Flower, fruit and leaf.
861. *Romanzoffia unalaschcensis* Cham. Flower and fruit.
862. *Phacelia franklinii* (R.Br.) Gray. Leaf, flower and fruit.
863. *Phacelia mollis* Macbr. Leaf and flower.

PLATE XXXVI


839
840
841
842
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PLATE XXXVII

Scale in millimeters.

FIG.

864. *Lappula myosotis* Moench. Nutlet.
865. *Lappula redowskii* (Hornem.) Greene. Nutlet.
866. *Mertensia maritima* (L.) S. F. Gray. Leaf, flower and nutlet.
867. *Mertensia paniculata* (Ait.) Don. Leaf, flower and nutlet.
868. *Myosotis alpestris asiatica* Vesterg. Leaf, limb of corolla, nutlet and fruiting calyx.
869. *Eritrichium aretioides* (C. & S.) DC. Leaf, flower and nutlet.

870A. *Amsinckia menziesii* (Lehm.) Nels & Macbr. Nutlet.

870B. *Amsinckia lycopsoides* Lehm. Nutlet.

871. *Plagiobotrys cognatus* (Greene) Johnst. Leaf, fruiting calyx and nutlets.
872. *Cryptanthe torreyana* (Gray) Greene. Leaf, calyx and nutlets.
873. *Lycopus uniflorus* Michx. Leaf and calyx.
874. *Lycopus lucidus* Turcz. Leaf, calyx and group of nutlets.
875. *Mentha arvensis* L. Leaf, calyx and nutlet.
876. *Scutellaria galericulata* L. Leaf and flower.
877. *Dracocephalum parviflorum* Nutt. Leaf, fruiting calyx and nutlet.
878. *Prunella vulgaris lanceolata* (Barton) Hult. Leaf, calyx and nutlet.
879. *Stachys palustris pilosa* (Nutt.) Epling. Leaf and calyx.
880. *Galeopsis bifida* Boenn. Leaf, calyx and nutlet.
881. *Pentstemon diffusus* Dougl. Calyx and leaf.
882. *Pentstemon gormanii* Greene. Leaves and fruit.
883. *Pentstemon procerus* Dougl. Leaf, flower and fruit.
884. *Collinsia parviflora* Dougl. Flower and leaf.
885. *Mimulus guttatus* DC. Leaves and flower.
886. *Mimulus lewisii* Pursh. Leaf and flower.

PLATE XXXVII

PLATE XXXVIII

Scale in millimeters.

FIG.

887. *Limosela aquatica* Leaf, flower and fruit.
888. *Syntheris borealis* Pennell. Fruit and leaf.
889. *Veronica grandiflora* Gaertn. Flower and leaf.
890. *Veronica americana* (Raf.) Schwein. Leaf and fruit.
891. *Veronica tenella* All. Fruit and leaf.
892. *Veronica stelleri* Pall. Fruit and leaf.
893. *Veronica wormskjoldii* R. & S. Fruit and leaf.
894. *Veronica peregrina* var. *xalapensis* (H.B.K.) Pennell. Fruit and leaves.
895. *Lagotis glauca* Gaertn. Leaves and flower.
896. *Castilleja parviflora* Bong. Fruit and leaf.
897. *Castilleja pallida caudata* Pennell. Leaves and flower.
898. *Castilleja raupii* Pennell. Lower and upper leaves, and flower.
899. *Castilleja hyperborea* Pennell. Leaf and flower.
900. *Castilleja villosissima* Pennell. Leaves, corolla and capsule.
901. *Castilleja unalaschcensis* (C. & S.) Malte. Leaves and corolla.
902. *Castilleja miniata* Dougl. Leaf and flower.
903. *Castilleja hyetophila* Pennell. Leaf and flower.
904. *Euphrasia mollis* (Ledeb.) Wettst. Fruit and leaf.
905. *Euphrasia subarctica* Raup. Fruit, flower and leaf.
906. *Pedicularis capitata* Adams. Leaf and flower.
907. *Pedicularis sudetica* Willd. Leaf and flower.
908. *Pedicularis flammea* L. Flower and section of leaf.
909. *Pedicularis oederi* Vahl. Flower and section of leaf.
910. *Pedicularis lanata* Willd. Flower and section of leaf.
911. *Pedicularis langsdorfii* Fisch. Flower and section of leaf.

PLATE XXXVIII

PLATE XXXIX

Scale in millimeters.

FIG.

912. *Pedicularis lapponica* L. Flower and leaf.
913. *Pedicularis ornithorhynchus* Benth. Corolla and section of leaf.
914. *Pedicularis labradorica* Panzer. Flower and sections of leaves.
915. *Pedicularis parviflora* Smith. Flower and section of leaf.
916. *Pedicularis pennellii* Hult. Flower and section of leaf.
917. *Pedicularis chamissonis* Stev. Flower and section of leaf.
918. *Pedicularis verticillata* L. Flower and section of leaf.
919. *Rhinanthus minor groenlandicus* (Chab.) Neum. Leaf, seed and flower.
920. *Pinguicula villosa* L. Whole plant.
921. *Pinguicula vulgaris* L. Flower and basal rosette of leaves.
922. *Utricularia macrorhiza* LeConte. Flower and leaf.
923. *Utricularia intermedia* Hayne. Winter bud, bladders and leaf.
924. *Utricularia minor* L. Floyer and section of stem.
925. *Boschniakia rossica* (C. & S.) B. Fedisch. Flower with bract and capsule.
926. *Orobanche uniflora* (C. & S.) B. Fedisch. Flower and stem.
927. *Orobanche fasciculata* Nutt. Flower and part of stem.
928. *Plantago maritima juncoides* (Lam.) Hult. Leaf, fruit and seed.
929. *Plantago major* L. Leaf, seed and fruit.
930. *Plantago macrocarpa* C. & S. Leaf, fruit and seed.
931. *Plantago canescens* Adams. Leaf, fruit and seed.
932. *Galium boreale* L. Fruit and whorls of leaves.
933. *Galium kamtschaticum* Steller. Fruit and leaf.
934. *Galium aparine* L. Fruit and whorl of leaves.
935. *Galium triflorum* Michx. Fruit and leaf.
936. *Galium trifidum* L. Fruit with pedicel and whorl of leaves.
937. *Linnaea borealis americana* (Forbes) Hult. Flower and leaf.

PLATE XXXIX


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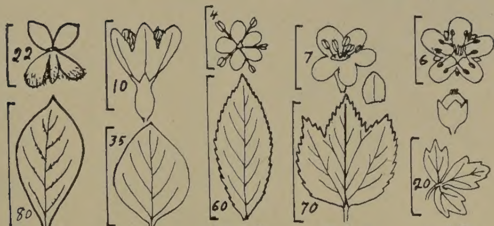
PLATE XL

Scale in millimeters.

FIG.

938. *Lonicera involucrata* (Rich.) Banks. Fruit and leaf.
939. *Symphoricarpus rivularis* Suksd. Flower and leaf.
940. *Sambucus racemosa pubens* (Michx.) Hult. Flower and leaflet.
941. *Viburnum edule* (Michx.) Raf. Flower, stone and fruit.
942. *Adoxa moschatellina* L. Flower, fruit and leaf.
943. *Valeriana capitata* Pall. Flower, seed and upper leaf.
944. *Valeriana sitchensis* Bong. Flower, seed and upper leaf.
945. *Campanula dasyantha* Bieb. Flower and leaf.
946. *Campanula aurita* Greene. Flower and leaves.
947. *Campanula uniflora* L. Flower, leaf and fruit.
948. *Campanula lasiocarpa* Cham. Flower and leaves.
949. *Campanula rotundifolia* L. Flower and leaves.
950. *Lobelia kalmii* Flower and leaves.

PLATE XL



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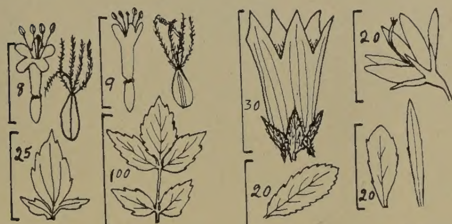

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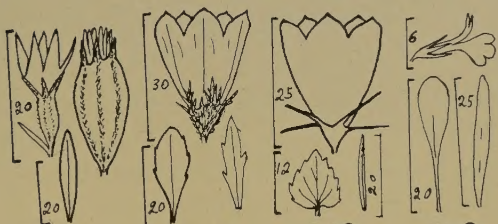

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